

Foreword

This 1981 doctoral thesis is posted on the ArXiv with explicit written permission of the Massachusetts Institute of Technology.

We post it here because of the following reasons:

- the Sc.D. thesis is referred to explicitly in a series of articles (see below);
- the initial chapters of the thesis contain still unpublished ideas and results that are relevant to ongoing discussions on fundamental problems in quantum theory, second-law violations, mixed versus pure or heterogeneous versus homogeneous ensembles, the nature of quantum states, entropy, irreversibility, entanglement, correlation, spontaneous decoherence, and related conceptual issues; we are currently actively working at extracting journal articles on this unpublished material;
- the last chapters introduce for the first time in the physics literature a nonlinear equation of motion for quantum dynamics which for all mixed states, including far-nonequilibrium, implies a general law of relaxation towards equilibrium along the “steepest entropy ascent” (or “maximal entropy generation”) trajectories in quantal state-space. The resulting nonlinear dynamics is compatible with the usual Hamiltonian Schrödinger-von Neumann description of interactions and energy conservation, as well as all the conditions listed in G.P. Beretta, “Nonlinear extensions of Schrödinger-von Neumann quantum dynamics: a set of necessary conditions for compatibility with thermodynamics,” *Mod. Phys. Lett.* **A20**, 977 (2005). In particular, for pure quantum mechanical states it reduces to the standard unitary Schrödinger-von Neumann evolution. Several publications based on this thesis have refined the mathematics and disclosed further intriguing features of the general dynamical law for irreversible processes (see below);
- being dated over twenty years ago, the publications based on this thesis may escape a superficial literature search, especially if based mainly on electronic search, because they are still unavailable for download in electronic format. We hope that posting the thesis will help to prevent further ‘rediscoveries’ such as that by Gheorghiu-Svirschevski (see references below). With the same intent to assure proper acknowledgements of previous fundamental and pioneering work in this area, the web site www.quantumthermodynamics.org now provides some reprints of these and other related publications.

To date, the thesis is referred to in the following references (for more references on “quantum thermodynamics” see www.quantumthermodynamics.org):

G.P. Beretta, “A general nonlinear evolution equation for irreversible conservative approach to stable equilibrium”, in *Frontiers of Nonequilibrium Statistical Physics*, proceedings of the NATO

Advanced Study Institute, Santa Fe, June 1984, edited by G.T. Moore and M.O. Scully, *NATO ASI Series B: Physics* **135**, Plenum Press, New York, p. 193 (1986);

G.P. Beretta, “Intrinsic entropy and intrinsic irreversibility for a single isolated constituent of matter: broader kinematics and generalized nonlinear dynamics”, in *Frontiers of Nonequilibrium Statistical Physics*, proceedings of the NATO Advanced Study Institute, Santa Fe, June 1984, edited by G.T. Moore and M.O. Scully, *NATO ASI Series B: Physics* **135**, Plenum Press, New York, p. 205 (1986);

G.P. Beretta, “On the relation between classical and quantum thermodynamic entropy”, *J. Math. Phys* **25**, 1507 (1984);

G.P. Beretta, E.P. Gyftopoulos, J.L. Park, and G.N. Hatsopoulos, “Quantum thermodynamics. A new equation of motion for a single constituent of matter”, *Nuovo Cimento* **B82**, 169 (1984);

G.P. Beretta, E.P. Gyftopoulos, and J.L. Park, “Quantum thermodynamics. A new equation of motion for a general quantum system”, *Nuovo Cimento* **B87**, 77 (1985);

G.P. Beretta, “Entropy and irreversibility for a single isolated two level system: new individual quantum states and new nonlinear equation of motion”, *Int. J. Theor. Phys.* **24**, 119 (1985);

G.P. Beretta, “Effect of irreversible atomic relaxation on resonance fluorescence, absorption, and stimulated emission”, *Int. J. Theor. Phys.* **24**, 1233 (1985);

G.P. Beretta, “A theorem on Lyapunov stability for dynamical systems and a conjecture on a property of entropy”, *J. Math. Phys* **27**, 305 (1986); the conjecture therein was later found proved in F. Hiai, M. Ohya, and M. Tsukada, *Pac. J. Math.* **96**, 99 (1981).

G.P. Beretta, “Steepest entropy ascent in quantum thermodynamics,” in *The Physics of Phase Space*, edited by Y.S. Kim and W.W. Zachary, *Lecture Notes in Physics* **278**, Springer-Verlag, New York, p. 441 (1986);

G.P. Beretta, “Quantum thermodynamics of nonequilibrium. Onsager reciprocity and dispersion-dissipation relations”, *Found. Phys.* **17**, 365 (1987);

S. Gheorghiu-Svirschevski, Addendum to “Nonlinear quantum evolution with maximal entropy production”, *Phys. Rev.* **A63**, 054102 (2001), see also *Phys. Rev.* **A63**, 022105 (2001);

G.P. Beretta, “Maximal-entropy-generation-rate nonlinear quantum dynamics compatible with second law, reciprocity, fluctuation–dissipation, and time–energy uncertainty relations”, arXiv:quant-ph/011204 (2001);

G.P. Beretta, “A nonlinear model dynamics for closed-system, constrained, maximal-entropy-generation relaxation by energy redistribution”, arXiv:quant-ph/0501178 (2005);

E.P. Gyftopoulos and G.P. Beretta, “What is the second law of thermodynamics and are there any limits to its validity?”, arXiv:quant-ph/0507187 (2005).

ON THE GENERAL EQUATION OF MOTION OF QUANTUM THERMODYNAMICS
AND
THE DISTINCTION BETWEEN QUANTAL AND NONQUANTAL UNCERTAINTIES

by
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Submitted to the Massachusetts Institute of Technology
on August 1, 1981 in partial fulfillment of the
requirements for the degree of Doctor of Science

ABSTRACT

A general quantum theory encompassing Mechanics, Thermodynamics and irreversible dynamics is presented in two parts.

The first part is concerned exclusively with the description of the states of any individual physical system. It is based on a new nonlinear quantum equation of motion, which reduces to the Schrödinger equation of motion of conventional quantum dynamics only under special conditions. It accounts for the implications of the laws of Thermodynamics as well as for irreversible phenomena, such as the natural tendency of an isolated system to transit from any non-equilibrium state to an equilibrium state of higher entropy. Conversely, the laws of Thermodynamics and irreversibility emerge as manifestations of the fundamental quantum dynamical behaviour of the elementary constituents of any material system. We call this part Quantum Thermodynamics.

The second part of the theory, which contains the first as a special case, is concerned with the description of stochastic distributions of states in an ensemble of identical physical systems each of which individually obeys the laws of Quantum Thermodynamics. It is based on a new measure-theoretic description of ensembles. It accounts unambiguously for the essential distinction between two types of uncertainties that are generally present in an ensemble, namely, quantal uncertainties due to the inherent quantal nature of the states of each individual member system and nonquantal uncertainties due to the stochastic distribution of states. We call this part Quantum Statistical Thermodynamics.

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Acknowledgements

It is a pleasure to acknowledge my indebtedness to those who have helped me in this work with many stimulating discussions and conversations.

My interest in the problems of the unification of Thermodynamics and Quantum Mechanics was stimulated by innumerable conversations with Professor Elias P. Gyftopoulos, M.I.T., throughout the 1979-80 academic year. My determination to address the irreversibility problem was originally stimulated by a lecture that Professor James L. Park, Washington State University, gave at M.I.T. in April 1979.

During the 1980-81 academic year I enjoyed many conversations on these problems with Professor Park (visiting M.I.T.) and Professor Gyftopoulos, my thesis supervisor. In several occasions I also enjoyed the enthusiastic and stimulating participation of Doctor George N. Hatsopoulos, president of the Thermo Electron Corporation.

Often, in these meetings, I have put on trial my results and extracted, from the subsequent discussions, ideas for further development. Specifically, I followed this pattern in refining and generalizing the equation of motion that is proposed here, the first embryo of which I had put on trial in early February 1981.

I am especially grateful to Professor Gyftopoulos also for his thorough critical revision of several drafts of the manuscript.

I am pleased to thank Professor James C. Keck, M.I.T., for his encouragement, support and critical help, and Professor Gian Carlo Rota, M.I.T., for his participation in my thesis committee.

This work was supported in part by a grant of the Thermo Electron Corporation.

Gian Paolo Beretta

Cambridge, August 1, 1981.

Chapter 1

INTRODUCTION

This dissertation has two objectives.

The first objective is to present a quantum theory of nature encompassing Mechanics, Thermodynamics and irreversible dynamics. This theory is concerned exclusively with the description of the states of any individual physical system. The objective is accomplished by generalizing the currently accepted formulation of quantum theory both as regards the description of the allowed states of an individual physical system and as regards the description of their causal evolution. This theory will be called Quantum Thermodynamics.

The second objective is to present an unambiguous statistical theory superimposed to Quantum Thermodynamics. This statistical theory is concerned with the description of stochastic distributions of states in an ensemble of identical physical systems each of which individually obeys the laws of Quantum Thermodynamics. The objective is accomplished by adopting a new measure-theoretic description of ensembles. This theory will be called Quantum Statistical Thermodynamics.

In the background is the work of G.N. Hatsopoulos and E.P. Gyftopoulos (1976). They assumed the laws of Thermodynamics as complementary to, consistent with, and independent of, the laws of Mechanics and formulated a unified quantum theory which encompasses within a single structure both Thermodynamics and Mechanics. This was accomplished by adjoining to the fundamental postulates of conventional quantum theory an additional independent postulate reflecting the essence of the laws of Thermodynamics. Three of their major conclusions can be stated as follows:

- (a) There exist quantum states of an individual physical system that are more general than those considered in conventional Quantum Mechanics.
- (b) The presently known law of causal evolution of quantum dynamics, based on the Schrödinger equation of motion, is incomplete. Not only it cannot describe irreversible processes but it cannot even describe some known reversible processes.
- (c) The distinction between states of an individual physical system and distributions of states in an ensemble of identical systems is essential. The unified quantum theory is concerned only with the states of an individual physical system. An unambiguous quantum statistical theory concerned with the distributions of states in an ensemble is presently lacking. Such a theory will be unambiguous if, and only if, it can uniquely account for the statistical composition of each ensemble, i.e. it unambiguously identifies both the spectrum of individual states represented in the ensemble and their relative population.

Conclusion (a) will be retained in this dissertation as a fundamental premise. Conclusions (b) and (c) motivate the two objectives of the dissertation.

As regards the first objective, Quantum Thermodynamics resolves the incompleteness of the present law of causal evolution. This is accomplished by postulating a new nonlinear equation of motion. The proposed equation of motion accounts for the implications of the laws of Thermodynamics, such as the existence of a unique stable equilibrium state of an individual system for any allowed set of initial values of its constants of the motion, as well as for irreversible phenomena, such as the tendency of an isolated system to transit from any initial non-equilibrium state to an equilibrium state of higher entropy. Moreover, it reduces to the Schrödinger equation of motion for a particular class of states. The resulting dynamical postulate of Quantum Thermodynamics replaces the dynamical and the additional independent postulates of the Hatsopoulos-Gyftopoulos unified quantum theory. Another novel characteristic of Quantum Thermodynamics is a substantial enlargement of the class of physical observable representatives to include nonlinear functionals of the state operator.

As regards the second objective, Quantum Statistical Thermodynamics resolves the present lack of an unambiguous quantum statistical theory. This is accomplished by assigning to each ensemble a measure-theoretic descriptor, called the statistical-weight measure, which represents the distribution of individual quantum thermodynamical states in the ensemble. Every statistical-weight measure admits of a unique spectral resolution into irreducible measures, called Dirac measures. Since each Dirac measure identifies a single quantum thermodynamical state, the corresponding coefficient in the spectral resolution of the statistical-weight measure represents the relative population, in the ensemble, of systems being in that individual quantum thermodynamical state. The unambiguity of Quantum Statistical Thermodynamics is ensured by the uniqueness of the spectral resolution of any statistical-weight measure. Consistently, Quantum Statistical Thermodynamics reduces to Quantum Thermodynamics for the class of statistical-weight measures that are themselves Dirac measures and correspond to ensembles composed of systems each of which is in exactly the same individual quantum thermodynamical state as all the other systems. Quantum Statistical Thermodynamics contains Quantum Thermodynamics in the same way as Classical Statistical Mechanics contains Classical Mechanics.

The dissertation is structured as follows:

Chapter 2 presents the background considerations motivating the present work, including: an inconsistency of the currently prevailing interpretation of the physical significance of Thermodynamics, the elimination of such inconsistency as achieved in the unified quantum theory of Mechanics and Thermodynamics proposed by Hatsopoulos and Gyftopoulos, two fundamental problems arising within that theory which are presently open and are addressed in the present work, and the premises from which we proceed to resolve the two fundamental problems.

Chapter 3 presents a general discussion on the concept of state of an individual system, including: a re-examination of its conceptual significance independently of the current formulation of quantum theory, the identification of the sources of ambiguity in the formulation of conventional Quantum Statistical Mechanics, and the conditions that a statistical theory must satisfy in order to be unambiguous. This discussion is based on the definitions of homogeneous preparations of a physical system, the rule of correspondence between the concept of individual state and that of homogeneous preparation, and the distinction between a physical and a statistical theory of nature.

Chapters 4 and 5 present the general quantum theory that we propose, including: the postulates of Quantum Thermodynamics, the postulates of Quantum Statistical Thermodynamics, and major theorems.

Chapter 6 concludes with a summary and recommendations for future studies.

Chapter 2

BACKGROUND

This Chapter presents the background considerations motivating the present work. In Section 2.1, the currently prevailing understanding of the physical significance of Thermodynamics is examined and shown to be inconsistent. It is then observed that within a recently proposed unified quantum theory of Mechanics and Thermodynamics, this inconsistency is eliminated. However, other important problems remain to be solved. In Section 2.2, the two fundamental problems addressed in this dissertation are outlined. Our approach to the solution of these problems is based on three independent premises that are explicitly stated at the end of the Chapter.

2.1 PHYSICAL SIGNIFICANCE OF THERMODYNAMICS

The prevailing interpretation of the physical significance of Thermodynamics, which is almost invariably proposed today, can be traced back to the works of J.C. Maxwell (1859), L.E. Boltzmann (1871) and J.W. Gibbs (1902), though the modern version has been filtered through the more recent ideas of Information Theory.

Thermodynamics is considered as a statistical theory of complex macroscopic systems. According to P. Glansdorff and I. Prigogine (1971), “the great importance of thermodynamic ... methods is that they provide us with a ‘reduced description’, a ‘simplified language’ with which to describe macroscopic systems.” Thus, Thermodynamics would be a particularly effective set of methods to treat complex macroscopic systems, whose mechanical description (“the” fundamental description) is practically too complicated and conceptually of little interest because the initial conditions are hardly reproducible. Moreover, for systems with a sufficiently large number of degrees of freedom, i.e. for complex macroscopic systems, the laws of Thermodynamics would be “derivable” from the fundamental mechanical description.

2.1.1 Prevailing View: Statistical Interpretation

According to the statistical (or information-theoretic) interpretation, the “thermodynamic state” of a system is conceived of as the best description of the state of knowledge of an observer possessing only partial information about the “actual state” in which the observed system actually is. Especially for macroscopic systems, there are so many possible “actual states”, that it would be fruitless, in addition to practically impossible, to know which one is actually realized.

The state of knowledge of the observer is represented by probabilities p_i assigned to each possible “actual state”. The assignment of such probabilities is based on an *additional postulate* adopted as a complement to the laws of Mechanics. The currently prevailing additional postulate is the *maximum “entropy” principle*, cf. E.T. Jaynes (1957). For reasons discussed in Chapter 4, we will call it the maximum “statistical uncertainty” principle. According to such postulate, the probabilities p_i should be assigned so as to maximize the *statistical uncertainty* of the observer consistently with whatever information is available to him. This method guarantees the least biased assignment. The indicator of statistical uncertainty, that is to be maximized, is that established by C.E. Shannon (1948) in the context of Information Theory, i.e.

$$I = - \sum_i p_i \ln p_i . \quad (2.1)$$

This indicator I is commonly called the “entropy” and identified with the concept of entropy as implied by the laws of Thermodynamics. The historical background of this statistical or information-theoretic interpretation of Thermodynamics, which includes the works of Maxwell, Boltzmann, Gibbs and Shannon, has been recently reviewed by Jaynes (1978).

The innumerable successes of the mathematical formula for the indicator of statistical uncertainty, or the “entropy”, have been interpreted as a guarantee of correctness of the attached statistical interpretation. However, E.P. Gyftopoulos and G.N. Hatsopoulos (1980) have shown that such an interpretation leads to an unacceptable inconsistency.

2.1.2 Inconsistency of the Statistical Interpretation

The inconsistency stems from the incompatibility of the premise that the thermodynamic state is a subjective characteristic of a partially informed observer, with a large body of experimental facts.

For example, it is an experimental fact that any observer can extract a net amount of work from a system in a non-equilibrium state without leaving other net effects external to the system. This the observer can do even if he is totally ignorant about the “actual states” of the system. This we do in fact when we extract work from a charged battery and yet ignore the “actual states” of the battery. The premise that the thermodynamic state is subjective, and a function of the knowledge of the observer, would instead lead to conclude, inconsistently with empirical experience, that no net amount of work can be extracted by a totally ignorant observer.

Again, it is an experimental fact that an isolated system in a non-equilibrium state generally proceeds irreversibly towards an equilibrium state. Such a process occurs in the system, not in the mind of the observer. Indeed, the amount of work that can be extracted from the system at the end of such a process has diminished, and there is nothing any observer can do to restore it without leaving net effects external to the system.

These examples belong to a body of experimental facts that are consistently regularized by the laws of Thermodynamics but are impossible to explain when its statistical interpretation is assumed. Hence, the statistical interpretation of the physical significance of Thermodynamics is inconsistent.

2.1.3 Elimination of the Inconsistency

G.N. Hatsopoulos and E.P. Gyftopoulos (1976) have indicated that the inconsistency can be eliminated by considering the laws of Thermodynamics as independent of and complementary to

the laws of Mechanics. They have developed an unified quantum theory encompassing within a single structure both Mechanics and Thermodynamics, in which the laws of Thermodynamics emerge as objective manifestations of the inherent quantal characteristics of any material system. Observers and their state of knowledge play no role in the theory. Hence, the inconsistency emerging from the premise that the thermodynamic state is subjective is eliminated.

The Hatsopoulos-Gyftopoulos unified quantum theory was developed by adjoining to the fundamental postulates of conventional quantum theory, an additional independent postulate reflecting the essence of the laws of Thermodynamics.

A fundamental implication of the unified quantum theory is that the class of quantum states of any individual physical system is broader than the class of quantum states considered in conventional Quantum Mechanics. Such a broader class of quantum states includes equilibrium and non-equilibrium states. The maximum amount of work that can be extracted from any system without leaving other net effects external to the system is solely a function of the quantum state of the system. If the system is in a stable equilibrium state, then no work can be extracted without leaving net effects external to the system. This is a statement of the impossibility of a perpetual motion machine of the second kind. If the system is in a non-equilibrium state, then the maximum amount of work that can be extracted is nonzero. This explains the body of experimental facts considered in the last Section.

The inconsistency is eliminated, however, two major problems remain open and motivate the present work. First, the presently known equation of motion of quantum dynamics is incomplete, because it cannot explain irreversible processes in addition to some known important reversible processes. Second, an unambiguous quantum statistical theory for the description of distributions of states in an ensemble of identical systems is presently lacking.

2.2 OPEN PROBLEMS AND PRESENT PREMISES

2.2.1 Lack of a Complete Equation of Motion

It is a well known fact of today's physics that any known *fundamental* description of the dynamical behavior of any physical system (complex or simple, macroscopic or microscopic) is reversible. This is a characteristic feature of classical Hamiltonian dynamics (i.e., the Hamilton equations of motion) as well as quantum Hamiltonian dynamics (i.e., the Schrödinger equation of motion). However, it is also well known that irreversibility dominates the empirical world. Hence, the Hamiltonian dynamical description of physical systems is incompatible with irreversible physical reality. Several rationalizations of this paradox have been proposed during the last century. All are based on the assumption that irreversibility is *not* an objective phenomenon inherent in the nature of material systems. For example, some view irreversibility as an "antropomorphic" concept expressing the ever increasing obsolescence of past information (cf. Jaynes (1957)). However, if the laws of Thermodynamics are understood as objective fundamental laws of nature, then these rationalizations cannot be conclusive.

Within the Hatsopoulos-Gyftopoulos unified quantum theory the paradox acquired a novel significance. A general theory encompassing the laws of Mechanics and Thermodynamics should account for all known reversible and irreversible processes. If the known equations of motion cannot account for some known process, then they are incomplete. For example, the Schrödinger equation of motion is incomplete. We will return to this point in Chapter 5.

To resolve the incompleteness of the present dynamical theory, we will proceed from the premise

that irreversibility should be explained as a fundamental physical phenomenon due to the inherent dynamical nature of the elementary constituents of any material system and the premise that the laws of Thermodynamics should follow as theorems of a complete dynamical theory.

2.2.2 Lack of an Unambiguous Quantum Statistical Theory

The distinction between *state* of an individual physical system and stochastic *distribution of states* in an ensemble of identical physical systems is essential to the Hatsopoulos-Gyftopoulos unified quantum theory of Mechanics and Thermodynamics. The theory is in fact concerned only with a fundamental description of the states of any individual physical system.

A quantum statistical theory capable of describing unambiguously distributions of states in an ensemble of identical systems is presently not available. Yet, such a theory would be of theoretical importance to clarify the physical significance of the unified quantum theory and of practical importance to provide the ground for a description of situations in which maximal theoretical information on the state of a system is not available and the methods of statistical inference must be used.

A statistical theory will be unambiguous if, and only if, it can uniquely account for the statistical composition of each ensemble, i.e. it unambiguously identifies both the spectrum of states represented in the ensemble and their relative population. The physical importance of this requirement can be clarified as follows. A well known striking conclusion of conventional quantum theory, which has been enhanced by the unified quantum theory, is the existence of uncertainties, that we call *quantal uncertainties*, which are inherent in the nature of the states of any individual physical system. In addition to this type of uncertainties, a quantum statistical theory must also take into account an independent type of uncertainties, that we call *nonquantal uncertainties*, originating from the fact that in general the member systems of an ensemble are stochastically distributed over a range of different individual states. The theory is unambiguous if and only if it provides a description of ensembles which maintains the essential distinction between quantal and nonquantal uncertainties. For example, we will see that conventional Quantum Statistical Mechanics does not satisfy this requirement and is therefore ambiguous.

Implicit in the foregoing discussion is the premise that the concept of state of an individual physical system is fundamental in a theory of nature. In other words, it should be always possible to think of any individual physical system as being in some definite state. To resolve the present lack of an unambiguous statistical quantum theory, we will proceed in Chapter 3 by capitalizing on this premise.

2.2.3 Premises of the Present Work

Our objective in this dissertation is to solve the two fundamental problems just outlined, while retaining the successful achievements of the Hatsopoulos-Gyftopoulos unified quantum theory of Mechanics and Thermodynamics. The following statements summarize the premises of our approach:

- (a) The enlargement of the class of quantum states of any individual physical system, which has been introduced in the unified quantum theory, should be retained, since it is essential to explain consistently the laws of Thermodynamics as fundamental laws of nature.

- (b) The concept of state of an individual system is fundamental. It should be always possible to think of any individual system as being in some definite state. A quantum statistical theory should include such a concept without ambiguities.
- (c) The equation of motion of Hamiltonian dynamics (i.e., the Schrödinger equation) is incomplete; therefore, a new complete equation of motion is needed. A complete dynamical theory should explain irreversibility as a fundamental physical phenomenon and should entail the laws of Thermodynamics as theorems.

From these premises we proceed to develop a general quantum theory in which the two problems just outlined have a consistent solution.

Chapter 3

CONCEPT OF STATE OF AN INDIVIDUAL SYSTEM

This Chapter presents a general discussion on the concept of state of an individual physical system. In classical theory, this concept is well understood and established, and it plays a fundamental role, since every system is thought of as always being in some definite individual state. We will hypothesize that the concept can play a fundamental role even in quantum theory. We will see that within the formulation of conventional Quantum Statistical Mechanics, the concept of state of an individual system is ambiguously represented. Therefore, we shall conclude that conventional quantum theory is incomplete, since it lacks of a statistical quantum theory representing unambiguously this fundamental concept.

That in conventional Quantum Statistical Mechanics the concept of individual state is ambiguously represented, has been clearly shown by J.L. Park (1968a) (cf. Section 3.2.2). However, Park concluded: “Thus the concept of individual quantum state is fraught with ambiguity and should therefore be avoided in serious philosophical inquiries concerning the nature of quantum theory ... A quantum system should be regarded as never being in any physical state.” On the contrary, here we take the position that the concept of individual physical state is fundamental. From this premise, we conclude that what is fraught with ambiguity is not the concept of individual state, but rather the current mathematical formulation of Quantum Statistical Mechanics. Therefore, a serious reformulation of quantum theory is in order.

To pursue this objective, we proceed as follows. We re-examine the concept of state of an individual system independently of the formulations of either conventional quantum theory or the Hatsopoulos-Gyftopoulos unified quantum theory. In the light of this re-examination, we study the physical and statistical formulations of both classical theory and conventional quantum theory and review the ambiguity of conventional Quantum Statistical Mechanics. Finally, we identify necessary conditions that a statistical theory must satisfy in order to achieve an unambiguous representation of the concept of state of an individual system. Using these conditions, we shall be able to show (Chapter 4) that the statistical part of the general quantum theory that we propose is unambiguous.

3.1 RULES OF CORRESPONDENCE AND DEFINITION OF PARADIGM

A scientific theory of nature comprehends three realms:

- the realm of empirical experience (perceptions)
- the realm of theoretical constructs (conceptions)
- the realm of mathematical descriptions (representations).

The essence of the theory resides in the *links* that it establishes between elements of these three realms.

The links between perceptions and conceptions have been called *rules of correspondence* by H. Margenau (1950): “The rules of correspondence ... are not eternally grounded in the nature of things, nor are they immediately suggested by sensory experience; they are important parts of every theory of nature and receive their validity from the consistency, the internal neatness and success of the entire explanatory scheme.”

The rules of correspondence are normally defined through the mathematical formulation of the theory. Practitioners do not work with perceptions, conceptions and rules of correspondence expressed by verbose locutions. Rather, they work with data, mathematical entities and mathematical relations, i.e. with *mathematical descriptions* of perceptions, conceptions and rules of correspondence. The mathematical formulation is essential in giving structure to the theory; however, it is not generally unique. A theory might admit of several different, but mathematically equivalent, formulations.

A set of postulates giving (in their unity) structure to a theory, by linking theoretical constructs and rules of correspondence to mathematical descriptors and mathematical relations, can be called the *paradigm* of the theory. This terminology has been used by T.S. Kuhn (1962), in his book on The Structure of Scientific Revolutions.

The following two Sections are intended to present our general, non-mathematical re-examination of the concept of state of an individual system, based on the definition of the fundamental rules of correspondence between *states*, *homogeneous ensembles* and *homogeneous preparations*.

3.1.1 States and Homogeneous Ensembles

As discussed by J.L. Park (1968a), the dominant theme of quantum theory is the necessity to accept that the notion of state involves probabilistic concepts in an essential way. In quantum theory the links between *probabilities* and the empirical world are implicitly defined by established practices of experimental science: the construct probability is linked to the relative frequency in an *ensemble*. Thus the primary connection of a quantum theory of nature to the empirical world is through ensembles.

The purpose of a quantum theory is to regularize purely probabilistic information about the measurement results from a real ensemble of identical systems. A *real ensemble* is either an aggregate of identically prepared systems upon which measurements are performed or a sequence of measurements performed on a single system identically reprepared prior to each measurement, or a combination of both.

An important scheme for the classification of ensembles, especially emphasized by J. von Neumann (1932), hinges upon the concept of ensemble homogeneity. Given an ensemble it is always possible to conceive of it as subdivided into many subensembles.

Definition: Homogeneous Ensembles

An ensemble is said to be homogeneous if, and only if, every conceivable subdivision results into subensembles all identical to the original.

Here, two ensembles of identical systems are said to be *identical* if, and only if, the arithmetic mean value of data yielded by measurements of a physical observable on the member systems of one of the two ensembles is equal to the mean value of data yielded by measurements of the same physical observable on the member systems of the other ensemble, for *all conceivable* physical observables.

Since, by definition, there exist no subdivisions of a homogeneous ensemble into *different* subensembles, it follows that each individual member system of a homogeneous ensemble has exactly the same *intrinsic characteristics* as any other member. For, if all member systems did not have the same intrinsic characteristics, then it would be possible to conceive of subdivisions of the ensemble into subensembles that are not identical.

The whole of these intrinsic characteristics, shared by all the individual members systems of a homogeneous ensemble, defines the concept of *state* of an individual system. In short, a homogeneous ensemble is a real aggregate of identical systems each individually in the same state. Thus, the concept of state acquires physical meaning in its reference to the *individual system*, though its empirical correspondent is a homogeneous ensemble of identical systems. In fact, we can now express the rule of correspondence linking the physical concept of state to the empirical world:

The empirical correspondent of the theoretical concept of state of an individual system is a particular kind of ensemble: the *homogeneous ensemble*.

The power of this rule of correspondence is that it holds with the same fundamental meaning whether the concept of state does or does not involve probabilistic concepts.

3.1.2 Preparations and Ensembles

The act of generating an ensemble consists of the repeated application, on the member systems, of a list of operations called an ensemble preparation scheme or, simply, a *preparation*. By definition, a preparation must be *reproducible* in that it must be identically applied to all the members that are to form the ensemble.

It is noteworthy that the act of generating an ensemble, i.e. the concept of *preparation*, does not necessarily involve an interaction with the member systems of the ensemble itself. It is only the following *measurement* act which must necessarily involve an interaction. The concepts of preparation and measurement must not be confused (cf. H. Margenau and J.L. Park (1973)). A measurement act is an “operation performed on a system for the purpose of obtaining a numerical value which can, by virtue of the chosen experimental arrangement, be assigned to some definite, nameable observable.” A preparation scheme is instead any set of operations selected for the purpose of obtaining a real ensemble of identical systems. Thus a preparation is a scheme to “accept” systems upon which to perform measurements.

Deliberately, the concept of preparation as just defined is quite broad and unrestricted. In general, not all preparations generate homogeneous ensembles. If a preparation generates a homogeneous ensemble, it will be called a *homogeneous preparation*, otherwise, it will be called a *heterogeneous preparation*.

It is useful to define a shorthand notation to represent the notion of *statistical composition* of two, or more, preparation schemes. Let Π_1 and Π_2 represent two preparation schemes for a physical system. If the system is prepared according to scheme Π_1 with statistical weight w_1 or according to scheme Π_2 with statistical weight w_2 (where $w_1 + w_2 = 1$ and $w_1, w_2 > 0$), then we indicate the resulting composite preparation scheme Π by writing

$$\Pi = w_1\Pi_1 + w_2\Pi_2 ,$$

where this expression must be understood exclusively as a shorthand symbolic notation having no other meaning than that just cited. With this notation, and by the definition of homogeneous ensemble, we can give an alternative definition of homogeneous preparation.

Definition: Homogeneous Preparations

A preparation scheme is said to be homogeneous if, and only if, it cannot result from the statistical composition of different preparation schemes, i.e. if, and only if, any conceivable decomposition of the type

$$\Pi = w_1\Pi_1 + w_2\Pi_2 \quad \text{with } w_1, w_2 > 0$$

implies that $\Pi_1 = \Pi_2 = \Pi$.

As seen in the last Section, to the theoretical concept of *state* of an individual system is linked the empirical concept of *homogeneous ensemble*, which, in turn, has been linked here to the theoretical concept of *homogeneous preparation*. Thus the two theoretical concepts of *state* and *homogeneous preparation* are linked through their correspondence with the *homogeneous ensemble*. If the concept of state of an individual system is fundamental to the particular theory of nature under consideration, then so is the concept of homogeneous preparation. The two concepts are linked one-to-one regardless of the particular mathematical formulation of the theory. This is the conclusion of our re-examination of the concept of state of an individual system. The foregoing analysis has followed closely the analysis of J.L. Park (1968a). However, our conclusion is different, since, as we already discussed, our premise is to consider the concept of individual state as fundamental, regardless of the current formulation of quantum theory.

The importance of the notion of homogeneity, especially in the framework of quantum theory, has been emphasized by several authors, starting with J. von Neumann (1932). G. N. Hatsopoulos and E. P. Gyftopoulos (1976) have proposed a unified quantum theory of Mechanics and Thermodynamics requiring such a notion in a fundamental way. Their theory is concerned exclusively with a description of the homogeneous preparations, i.e. the individual states, of a physical system. The class of individual quantum states which are considered in their unified quantum theory is broader than the class of states considered by von Neumann. To underline this distinction, they adopted the term *unambiguous* preparation instead of homogeneous preparation. In the general quantum theory that we propose in Chapters 4 and 5, the Hatsopoulos-Gyftopoulos broader class of individual quantum states is maintained; however, also the term homogeneous preparation is maintained, since we have shown that the concept of homogeneity stands independently of the particular theory of nature under consideration.

3.2 PHYSICS VERSUS STATISTICAL PHYSICS

Physics is that branch of the theory of nature which is intended to describe within a causal framework the *states* of any physical system. Equivalently, the objective of physics is a description of the *homogeneous preparations* of a general physical system. To the concept of state, the physical

theory generally associates a *mathematical descriptor*, usually an element of a set. The same mathematical entity is thus also associated with the corresponding homogeneous preparation and the corresponding homogeneous ensemble.

Statistical physics is that branch of the theory of nature which is intended to describe within a statistical framework the distributions of states in an ensemble of identical systems each of which individually obeys the laws of the physical branch of the theory. Equivalently, the objective of statistical physics is a statistical description of *all possible preparations* of a physical system. To the concept of preparation, regardless of its homogeneity, the statistical theory generally associates a mathematical descriptor. The same descriptor is thus associated with the corresponding ensemble.

The typical construction pattern is to first formulate physics and then superimpose a statistical theory to it. Thus, first a physical theory of *homogeneous preparations* (states) is developed and then a statistical theory is superimposed to it for the description of any *preparation*, regardless of its homogeneity.

This pattern is exemplified in the next Sections, by reviewing classical theory – composed of the paradigms of Classical Mechanics and Classical Statistical Mechanics – and conventional quantum theory – composed of the paradigms of Quantum Mechanics and Quantum Statistical Mechanics.

Throughout this dissertation, the postulates forming the paradigms of different theories are identified by monograms of the type

PnNT: title

where Pn stands for “Postulate number n”, NT stands for the “Name of the Theory” and the title indicates the concept which is being given a mathematical description.

3.2.1 Classical Mechanics vs Classical Statistical Mechanics

The following review serves to clarify the role that the notions introduced in the foregoing discussion play in the classical theory of nature. It is presented here because this is the *only* complete (i.e., physical and statistical) theory of nature which is free of ambiguities. Its failure is not due to logical inconsistencies within the theory itself, but rather to its inability to regularize a class of empirical phenomena.

CLASSICAL MECHANICS

P1CM: Systems

To every physical *system* there corresponds a real phase-space Ω whose elements are points with coordinates indicated by $(\underline{q}, \underline{p})$.

P2CM: Homogeneous Preparations

To every *homogeneous preparation* scheme Π for a system, there corresponds a point $(\underline{q}, \underline{p})$ in the phase-space Ω of the system.

P3CM: Physical Observables

Some real functions g, h, \dots defined on Ω correspond to *physical observables* of the system. Given an ensemble of identical systems prepared according to the homogeneous scheme Π , with corresponding point $(\underline{q}, \underline{p})$ in phase-space, the arithmetic *mean value* \overline{g} of data yielded by measurements of the observable g is given by the value of the function g at the point $(\underline{q}, \underline{p})$, namely,

$$\overline{g} = g(\underline{q}, \underline{p}) .$$

P4CM: States

Every individual system is always in a *state* described by some point $(\underline{q}, \underline{p})$ in the corresponding phase-space.

P5CM: Causal Evolution

For every physical system there exists a function h (the Hamiltonian function), defined on the phase-space of the system, which determines the *causal evolution* of the state descriptor $(\underline{q}, \underline{p})$ via the following law (Hamilton's equations of motion)

$$\frac{d\underline{q}}{dt} = \frac{\partial h}{\partial \underline{p}} \quad \frac{d\underline{p}}{dt} = - \frac{\partial h}{\partial \underline{q}} . \quad (3.1)$$

This formulation of Classical Mechanics is non-orthodox, especially as regards postulates P2CM and P3CM. It has been adopted here in order to maintain a parallel structure with the formulations of other theories considered in the dissertation, and to exemplify the role played by the concept of homogeneous preparation in this well established theory of nature.

CLASSICAL STATISTICAL MECHANICS

P1CSM: Systems

Same as P1CM.

P2CSM: Preparations

To every *preparation* scheme Π for a system, there corresponds a continuous, real, positive function f defined on the phase-space Ω of the system, satisfying the normalization condition

$$\int_{\Omega} f(\underline{q}, \underline{p}) d\underline{q} d\underline{p} = 1 . \quad (3.2)$$

The function f is called the *density-of-phase function*.

P3CSM: Physical Observables

Some real functions g, h, \dots defined on Ω correspond to *physical observables* of the system. Given an ensemble of identical systems prepared according to the scheme Π , with corresponding density-of-phase function f , the *expected mean value* $\langle \bar{g} \rangle$ of measurements of the observable g is given by the following integral functional

$$\langle \bar{g} \rangle = \int_{\Omega} f(\underline{q}, \underline{p}) g(\underline{q}, \underline{p}) d\underline{q} d\underline{p}. \quad (3.3)$$

P4CSM: States

Same as P4CM.

P5CM: Causal Evolution

Same as P5CM. The corresponding evolution of the preparation descriptor (i.e. of the density-of-phase function f) is given by the equation (Liouville's equation)

$$\frac{df}{dt} = \{h, f\} \quad (3.4)$$

where $\{ , \}$ represents the Poisson bracket.

Some theorems of Classical Statistical Mechanics are as follows. Our conclusion from these theorems will be that Classical Statistical Mechanics provides an *unambiguous* description of preparations, regardless of their homogeneity.

Th1CSM

Among all the normalized functions definable on the phase-space Ω , only the Dirac delta “functions” $\delta_0(\underline{q}, \underline{p}) = \delta(\underline{q} - \underline{q}_0) \delta(\underline{p} - \underline{p}_0)$ are *irreducible*, in the sense that the equality

$$\delta_0(\underline{q}, \underline{p}) = w_1 f_1(\underline{q}, \underline{p}) + w_2 f_2(\underline{q}, \underline{p}) \text{ with } w_1, w_2 > 0 \quad (3.5)$$

holds if, and only if, $f_1 = f_2 = \delta_0$.

This follows from the fact that the Dirac delta function has a *support* (i.e., that part of the phase-space for which the function is nonzero) which is indivisible, being a single point $(\underline{q}_0, \underline{p}_0)$.

Th2CSM

To every distinct point $(\underline{q}_0, \underline{p}_0)$ in Ω there corresponds a distinct Dirac delta function $\delta(\underline{q} - \underline{q}_0) \delta(\underline{p} - \underline{p}_0)$ defined on Ω .

This theorem establishes a one-to-one correspondence between Dirac delta functions on phase-space and the state descriptors of Classical Mechanics, i.e. the points in phase-space.

Definition: Homogeneous Preparations within CSM

A preparation is said to be homogeneous if, and only if, it is represented by a Dirac delta function.

Th3CSM

Among all the preparation schemes for a physical system, only the *homogeneous* preparations cannot be conceived of as the result of a statistical composition of *different* preparation schemes. Moreover, each homogeneous preparation corresponds to one and only one *state* of an individual system, and vice versa.

This theorem discloses that the *rule of correspondence* linking the concept of state of an individual system to the concept of homogeneous preparation is indeed reproduced within the paradigm of Classical Statistical Mechanics.

Th4CSM

Every normalized function f defined on Ω can be uniquely expressed as a “weighted sum” of Dirac delta functions, i.e.

$$f(\underline{q}, \underline{p}) = \int_{\Omega} \delta(\underline{q} - \underline{q}_0) \delta(\underline{p} - \underline{p}_0) f(\underline{q}_0, \underline{p}_0) d\underline{q}_0 d\underline{p}_0 \quad (3.6)$$

where the function $f(\underline{q}_0, \underline{p}_0)$ itself represents the “weight” of the corresponding Dirac delta function. Consequently, every heterogeneous preparation can be *uniquely resolved* into its homogeneous component preparations.

This last theorem states explicitly that the mathematical descriptor of a heterogeneous preparation is *uniquely* indicative of the statistical structure of the preparation itself, i.e. of its homogeneous component preparations and the associated statistical weights. It is therefore correct, within the framework of this theory, to conceive of an individual system, which has been prepared according to a heterogeneous preparation, as being “in” a *state* corresponding to one of the homogeneous component preparations, with a probability given by the associated statistical weight.

To summarize, we have exemplified the key role played by the distinction between homogeneous and heterogeneous preparations within the framework of the classical theory of nature. The *link* between homogeneous preparations and states of an individual system is indeed reproduced in the theory. Moreover, the *concept* of state of an individual system is unambiguously represented even when the preparation scheme is heterogeneous.

3.2.2 Quantum Mechanics vs Quantum Statistical Mechanics

We now turn to the currently accepted version of conventional quantum theory – composed of the paradigms of Quantum Mechanics and Quantum Statistical Mechanics – and show that, within this formulation, the notion of state of an individual system is ambiguously represented. The structure of the paradigms is mathematically equivalent to the general structure outlined by J.L. Park (1968b).

QUANTUM MECHANICS

P1QM: Systems

To every physical *system* there corresponds a separable, complex Hilbert space \mathcal{H} whose elements are vectors ψ . The Hilbert space of a system composed of two distinguishable subsystems 1 and 2, with corresponding Hilbert spaces $\mathcal{H}(1)$ and $\mathcal{H}(2)$, is the direct product Hilbert space $\mathcal{H}(1) \otimes \mathcal{H}(2)$.

P2QM: Homogeneous Preparations

To every *homogeneous preparation* scheme Π for a system, there corresponds a unit-norm vector ψ in the Hilbert space of the system. The vector ψ is called the *state vector*.

P3QM: Physical Observables

Some linear, Hermitian operators G, H, \dots defined on \mathcal{H} correspond to *physical observables* of the system. Given an ensemble of identical systems prepared according to the homogeneous scheme Π , with corresponding state vector ψ , the arithmetic *mean value* \bar{g} of data yielded by measurements of the observable G is given by the value of the following scalar product

$$\bar{g} = \langle \psi, G\psi \rangle. \quad (3.7)$$

P4QM: States

Every individual system is always in a *state* described by some vector ψ in the corresponding Hilbert space.

P5QM: Causal Evolution

For every physical system there exists an operator H (the Hamiltonian operator), defined on the Hilbert space of the system, which determines the *causal evolution* of the state descriptor ψ via the following law (Schrödinger's equation of motion)

$$\frac{d\psi}{dt} = -\frac{i}{\hbar} H\psi. \quad (3.8)$$

The above paradigm has been constructed so as to entail the famous uncertainty theorem (W. Heisenberg (1927)). Mathematically, the theorem follows immediately from the Cauchy-Schwarz inequality applied to the scalar product $\langle \cdot, \cdot \rangle$. Let the variance of measurement results for the physical observable G be defined by

$$\text{var}(G) = \overline{(g - \bar{g})^2} = \langle \psi, G^2\psi \rangle - (\langle \psi, G\psi \rangle)^2. \quad (3.9)$$

The uncertainty theorem consists of the following well known general inequality valid for any two Hermitian operators G and F and therefore for two physical observables of the system

$$\text{var}(G)\text{var}(F) \geq |\langle \psi, [F, G]\psi \rangle|^2 \quad (3.10)$$

where $[,]$ is the standard commutator symbol ($[F, G] = FG - GF$). Conversely, the theory reflects the *fundamental Heisenberg hypothesis*, namely, that *inherent in the nature of the state* of any individual physical system there exist *uncertainties*. These uncertainties induce irreducible dispersions in the results of measurements performed on any *homogeneous* ensemble. No dispersionless ensemble can even be *conceived* within the framework of Quantum Mechanics. This striking conclusion constitutes one of the essential aspects of the departure of Quantum Mechanics from Classical Mechanics. The existence of uncertainties intimately connected with the nature of the state of any individual material system is a universally accepted aspect of today's physics.

QUANTUM STATISTICAL MECHANICS

P1QSM: Systems

Same as P1QM.

P2QSM: Preparations

To every *preparation* scheme Π for a system, there corresponds a linear, Hermitian, nonnegative-definite, unit-trace operator W defined on the Hilbert space of the system. The operator W is called the *statistical operator*.

P3QSM: Physical Observables

Some linear, Hermitian operators G, H, \dots defined on \mathcal{H} correspond to *physical observables* of the system. Given an ensemble of identical systems prepared according to the scheme Π , with corresponding statistical operator W , the *expected mean value* $\langle \bar{g} \rangle$ of measurements of the observable G is given by the value of the following trace functional

$$\langle \bar{g} \rangle = \text{Tr}(WG). \quad (3.11)$$

P4QSM: States

There can be no “P4” postulate. Saying that every individual system is always in a *state*, described by some vector ψ in \mathcal{H} , leads to inconsistencies and paradoxes (see the discussion at the end of this Section).

P5QSM: Causal Evolution

Same as P5QM. The corresponding evolution of the preparation descriptor (i.e., of the statistical operator W) is given by the equation (von Neumann's equation)

$$\frac{dW}{dt} = -\frac{i}{\hbar}[H, W]. \quad (3.12)$$

It is noteworthy that the *statistical operator* W (which is also usually called the *density operator* and indicated by the symbol ρ) has an essentially different physical meaning than the *state operator* defined within the paradigm of Quantum Thermodynamics. This distinction will be clarified in Section 4.1.1.

Some of the theorems of Quantum Statistical Mechanics are as follows.

Th1QSM (J. von Neumann (1932))

Among the linear, Hermitian, nonnegative-definite, unit-trace operators W definable on the Hilbert space \mathcal{H} , only the projection operators P_ψ onto the one-dimensional subspaces of \mathcal{H} are *irreducible*, in the sense that the equality

$$P_\psi = a_1 W_1 + a_2 W_2 \quad \text{with} \quad a_1, a_2 > 0 \quad (3.13)$$

holds if, and only if, $W_1 = W_2 = P_\psi$.

This follows from the fact that the projection operators P_ψ onto the one-dimensional subspaces of \mathcal{H} are the extreme elements of the convex set of statistical operators on \mathcal{H} .

Th2QSM

To every distinct unit-norm vector ψ in \mathcal{H} there corresponds a distinct projection operator P_ψ onto the one-dimensional subspace of \mathcal{H} spanned by ψ .

This theorem establishes a one-to-one correspondence between projection operators onto one-dimensional subspaces of the Hilbert space and the state descriptors of Quantum Mechanics, i.e. the state vectors in Hilbert space.

Definition: Homogeneous Preparations within QSM

A preparation is said to be homogeneous if, and only if, it is described by a projection operator P_ψ onto a one-dimensional subspace of \mathcal{H} .

Th3QSM

Among all the preparation schemes for a physical system, only the *homogeneous* preparations cannot be conceived as the result of a statistical composition of *different* preparation schemes. Moreover, each homogeneous preparation corresponds to one and only one *state* of an individual system, and vice versa.

This theorem discloses that the *rule of correspondence* linking the concept of state of an individual system to the concept of homogeneous preparation is indeed reproduced within the paradigm of Quantum Statistical Mechanics.

Th4QSM (E. Schrödinger (1936))

Every non-idempotent statistical operator W on \mathcal{H} (i.e., the statistical operators that are not projection operators onto one-dimensional subspaces of \mathcal{H}) can be expressed as a weighted sum of projection operators (onto one-dimensional subspaces of \mathcal{H}) in at least two different ways (generally, an infinity of ways), such as

$$W = \sum_n w_n P_{\psi_n} = \sum_q w'_q P_{\phi_q} = \dots \quad (3.14)$$

Consequence of this theorem is that the *concept* of state of an individual system is *not* unambiguously represented within Quantum Statistical Mechanics and, therefore, there can be no state postulate (P4QSM). In fact, if we insisted that such a postulate be included in the paradigm of the theory, a logical consequence of the last theorem would be that an individual system prepared according to the heterogeneous preparation scheme II, with corresponding statistical operator W , is, for example, in state ψ_n with probability w_n and, at the same time, in state ϕ_q with probability w'_q . Such a system is what J.L. Park (1968a) called a *quantum monster*: a single system which is concurrently “in” *two different* states.

This is the observation that led Park to the conclusion quoted at the beginning of this Chapter. We have already objected that the above ambiguity about the concept of state of an individual system should be charged to the underlying mathematical description rather than to the concept itself.

To summarize, this Section has exemplified the key role played by the distinction between homogeneous and heterogeneous preparations within the framework of the conventional quantum theory of nature. The *link* between homogeneous preparations and states of an individual system is reproduced. However, the *concept* of state of an individual system is ambiguously represented when the preparation scheme is heterogeneous.

To this point, we have established the scientific need to formulate a quantum statistical theory that includes the concept of state of an individual system without ambiguities.

3.2.3 Unambiguous Description of Heterogeneous Preparations

By examining the paradigms of Classical Statistical Mechanics and Quantum Statistical Mechanics, we have learned that a mathematical description of heterogeneous preparations must satisfy certain conditions in order to be considered unambiguous. We summarize the results by stating three necessary conditions which define explicitly the notion of unambiguous mathematical description of heterogeneous preparations.

A mathematical description of preparations is defined as follows:

- (o) To any preparation scheme there corresponds an element of the set of mathematical descriptors.

The three necessary conditions are as follows. Each condition is exemplified by indicating its realization within the paradigm of CSM, where the set of mathematical descriptors is the set of density-of-phase functions defined on the phase-space of the system.

- (i) To the concept of statistical composition of different preparation schemes there must correspond a mathematical *rule* to combine their mathematical descriptors so as to obtain the mathematical descriptor of the composite preparation. This rule of combination must be such that, for every physical observable, the expected mean value corresponding to the composite preparation equals the statistically weighted sum of the expected mean values corresponding to the component preparations.

Within CSM, to the statistical composition (with weights w_1 and w_2) of two preparations with corresponding density-of-phase functions f_1 and f_2 , there corresponds the following rule of combination yielding the density-of-phase function f_C of the composite preparation:

$$f_C = w_1 f_1 + w_2 f_2 .$$

It is immediate to verify that the requirement about the expected mean values is satisfied, i.e. that

$$\langle \bar{g} \rangle_C = w_1 \langle \bar{g} \rangle_1 + w_2 \langle \bar{g} \rangle_2 .$$

- (ii) To every homogeneous preparation there must correspond an *irreducible* mathematical descriptor, i.e. an element of the set of mathematical descriptors which cannot be obtained from the combination of *different* elements of the set. This implies not only that such irreducible elements must exist, but also that they must be at least as “numerous” as the different homogeneous preparations.

Within CSM, to every homogeneous preparation there corresponds a Dirac delta “function” which is indeed irreducible, since its support is a single point in phase-space. Moreover, a Dirac delta function can be defined in correspondence to every point in phase space (cf. theorem Th2CSM).

- (iii) To the uniqueness of resolution of any preparation into its homogeneous component preparations there must correspond the uniqueness of resolution of each mathematical descriptor into a combination of its irreducible components.

Within CSM, every density-of-phase function can be uniquely resolved into a “weighted sum” of irreducible Dirac delta functions (cf. theorem Th4CSM) .

The most demanding conditions are (ii) and (iii). Condition (ii) reflects the need for a correct mathematical correspondent to the concept of *homogeneous preparation*. The irreducibility of this class of preparations is essential and must therefore be reflected in the mathematical description. In addition, the description must be mathematically rich enough so that with every distinct homogeneous preparation is associated at least one distinct mathematical descriptor, thus reproducing the *rule of correspondence* between states and homogeneous preparations. Condition (iii) reflects the need for an unambiguous representation of the *concept* of state of an individual system prepared according to a heterogeneous preparation. The uniqueness of resolution of a heterogeneous preparation into its homogeneous component preparations is essential to avoid paradoxical conclusions of the type discussed in last Section, and must therefore be reflected in the mathematical description.

In our search for an unambiguous formulation of a statistical theory to be superimposed to Quantum Thermodynamics (cf. Section 4.1), three different mathematical descriptions of heterogeneous preparations were considered. When analyzed in the light of the conditions just defined, two were found unsatisfactory (these attempts are instructive and are outlined in appendix A), but the third satisfied all three conditions. This new description of preparations is proposed in Section 4.2.1 and then adopted in Section 4.2.2 to formulate the paradigm of Quantum Statistical Thermodynamics.

Chapter 4

NEW GENERAL QUANTUM THEORY: STATES AND STATISTICS

This Chapter presents a general quantum theory in which the concept of state of an individual system is unambiguously represented and which encompasses conventional Quantum Mechanics, Thermodynamics of stable equilibrium states and irreversible dynamics. Section 4.1 presents the paradigm of the physical part of the theory, that we call Quantum Thermodynamics. Section 4.2 presents the paradigm of the statistical part, that we call Quantum Statistical Thermodynamics.

4.1 QUANTUM THERMODYNAMICS

4.1.1 The paradigm of Quantum Thermodynamics

The paradigm of Quantum Thermodynamics is based on the following five postulates.

P1QT: Systems

Same as P1QM (Section 3.2.2).

Definition: Quantal Phase-domain

Let \mathcal{L} denote the real space of linear, Hermitian operators on the Hilbert space \mathcal{H} of the system, and \mathcal{P} the convex subset of \mathcal{L} of all linear, Hermitian, nonnegative-definite, unit-trace operators ρ . We call \mathcal{P} the *quantal phase-domain*.

P2QT: Homogeneous Preparations

To every *homogeneous preparation* scheme Π for a system, there corresponds an operator ρ in the quantal phase-domain \mathcal{P} of the system. We call ρ the *state operator*.

P3QT: Physical Observables

Some real functionals g, h, \dots defined on \mathcal{P} correspond to *physical observables* of the system. Given an ensemble of identical systems prepared according to the homogeneous scheme Π , with corresponding state operator ρ , the arithmetic *mean value* \bar{g} of data yielded by measurements of the observable g is given by the value of the functional g at the point ρ in the quantal phase-domain, namely,

$$\bar{g} = g(\rho).$$

P4QT: States

Every individual system is always in a *state* described by some state operator ρ in the corresponding quantal phase-domain.

P5QT: Causal Evolution

For every physical system there exists a superoperator \hat{N} (the evolution superoperator), defined on the Hilbert space of the system, which determines the *causal evolution* of the state descriptor ρ via the following law

$$\frac{d\rho}{dt} = \hat{N}(\rho). \quad (4.1)$$

The expression for the evolution superoperator \hat{N} is given in Chapter 5 (eq. 5.30). It differs substantially from the so-called Liouvillian superoperator \hat{L}_o (eq. 5.3).

It is noteworthy that to every real, *linear* functional g defined on \mathcal{L} (and therefore also on \mathcal{P}), there corresponds a unique linear, Hermitian operator G on \mathcal{H} such that $g(\rho) = \text{Tr}(G\rho)$, for every ρ . Thus, the representation of physical observables by means of linear, Hermitian operators (cf. the paradigm of Quantum Mechanics) is contained in the present formulation as a particular case. For example, the physical observable energy is represented here by the linear functional $h(\rho) = \text{Tr}(H\rho)$ where H is the standard Hamiltonian operator of the system. However, a new feature of the proposed paradigm, in addition to the introduction of the evolution superoperator \hat{N} , is that postulate P3QT has enlarged substantially the class of physical observable representatives, to include *nonlinear* functionals on \mathcal{P} . An example of nonlinear functional is $s(\rho) = -k\text{Tr}(\rho \ln \rho)$. As shown by G.N. Hatsopoulos and E.P. Gyftopoulos (1976) this nonlinear functional represents an important physical observable called the *entropy*.

It is also noteworthy that postulate P4QT, compared to P4QM, has enlarged substantially the class of mathematical state descriptors. Whereas Quantum Mechanics includes only the states that can be described by idempotent state operators (i.e., projection operators P_ψ onto the one-dimensional subspaces of \mathcal{H} spanned by the state vectors ψ), Quantum Thermodynamics includes states that are described by both idempotent and non-idempotent state operators. This enlargement of the class of state descriptors has allowed Hatsopoulos and Gyftopoulos to encompass within a single quantum theoretical structure both Mechanics and Thermodynamics.

An essential distinction must be noticed between the paradigm of Quantum Thermodynamics and that of Quantum Statistical Mechanics, specifically, the distinction between the *state operator* ρ and the *statistical* (or density) *operator* W (as defined in Section 3.2.2). Though these two operators have the same *mathematical* properties, they describe different concepts. A state operator ρ describes a *homogeneous* preparation scheme, while a statistical operator W describes any preparation scheme, regardless of its homogeneity. Indeed, Quantum Thermodynamics is a *physical* theory, while Quantum Statistical Mechanics is a *statistical* theory. Thus, the physical meaning attached to these two mathematically similar operators is completely different. However, within the present formulation, no confusion should arise, since no statistical or density operator is defined.

To complete the formulation of our general quantum theory, we need to superimpose a statistical theory to the paradigm of Quantum Thermodynamics.

Typically, a statistical theory deals with situations in which the preparation scheme is not homogeneous and, thus, there exists *uncertainty* about which homogeneous preparation scheme

is actually adopted to prepare the individual systems. Uncertainties of this type are *not* inherent in the nature of the individual states, rather, they are inherent in the nature of the preparation scheme and they are linked one-to-one to the heterogeneity of the scheme. The purpose of a statistical theory is to describe all preparation schemes and distinguish unambiguously between two types of uncertainties: quantal uncertainties associated with the quantal nature of the states of each individual system and nonquantal uncertainties associated with the heterogeneity of a preparation scheme. The next Section sharpens this distinction.

4.1.2 Quantal vs Nonquantal Uncertainties

Consider a heterogeneous preparation Π resulting from the statistical composition of different homogeneous schemes Π_n with corresponding statistical weights w_n . An *individual* system prepared according to such a preparation scheme is “actually” prepared according to the homogeneous scheme Π_n with probability w_n . From the postulates P2QT and P4QT of Quantum Thermodynamics, it follows that an individual system prepared according to the homogeneous scheme Π_n is “in” the *state* described by the corresponding state operator ρ_n . Therefore, an individual system prepared according to Π is in *state* ρ_n with probability w_n .

The probabilities w_n are characteristics of the heterogeneous preparation Π , having as empirical correspondents the relative populations, in a heterogeneous ensemble prepared according to Π , of systems whose individual state is ρ_n . It is clear that such probabilities are *not* inherent characteristics of the *state* of the individual member systems of the heterogeneous ensemble. Rather, they are characteristics of the *collection* of such individual systems, i.e. of the statistical structure of the ensemble considered as a whole. In short, the probabilities w_n reflect *uncertainties* that are inherent in the *heterogeneity* of the preparation scheme Π and are completely *independent* of the nature of the component *homogeneous* preparations ρ_n .

The following natural question arises: Is it possible to describe within a single formulation both nonquantal uncertainties of this type (not contemplated in Quantum Thermodynamics) and quantal uncertainties as implied by Quantum Thermodynamics, and yet maintain unambiguously reflected their essential distinction? In Section 3.2.3, we have answered to part of this question, by stating three necessary conditions that such a formulation must satisfy. These conditions have guided us in the formulation of the statistical theory proposed in the next Section, which constitutes an affirmative answer to the question.

4.2 QUANTUM STATISTICAL THERMODYNAMICS

Quantum Statistical Thermodynamics is the statistical part of the general quantum theory that we propose. It is concerned with the description of all preparations for a physical system or, equivalently, of distributions of states in any ensemble of systems each of which individually obeys the laws of Quantum Thermodynamics. It is based on a mathematical description of preparations which accounts unambiguously for the two types of uncertainties that are present in an ensemble generated by a heterogeneous preparation, namely, quantal and nonquantal uncertainties.

A statistical theory with these characteristics is presently lacking and, as we have seen, this fact is a source of conceptual difficulties. The formulation that we propose is based on a new measure-theoretic description of preparations.

4.2.1 Measure-theoretic Description of Preparations

This Section presents a mathematical description of preparations which satisfies the three necessary conditions stated in Section 3.2.3. The mathematical notion of *measure* defined on a set (cf., e.g., G. Fano (1971)) is the key notion on which the proposed description is based.

We recall that every point of the quantal phase-domain of a system is a state operator which, according to postulate P4QT of Quantum Thermodynamics, describes one of the possible states of an individual system or, equivalently, a homogeneous preparation for such a system.

We now postulate that the mathematical descriptor of a preparation scheme is a *measure* μ defined on the quantal phase-domain \mathcal{P} of the system, satisfying the following normalization condition

$$\mu(\mathcal{P}) = \int_{\mathcal{P}} \mu(d\rho) = 1. \quad (4.2)$$

We call μ the *statistical-weight measure*. In addition, we postulate that the expected value of a physical observable represented by the functional g , defined on \mathcal{P} , is given by

$$\langle \bar{g} \rangle = \int_{\mathcal{P}} g(\rho) \mu(d\rho). \quad (4.3)$$

We now examine the proposed description in the light of the conditions of Section 3.2.3. Condition (i) is satisfied by defining the rule of measure combination

$$\mu = \sum_n w_n \mu_n \quad (4.4)$$

corresponding to the concept of statistical composition of different preparations. In fact, the corresponding expected mean value of a generic observable, with corresponding functional g , is correctly given by

$$\begin{aligned} \langle \bar{g} \rangle &= \int_{\mathcal{P}} g(\rho) \mu(d\rho) = \int_{\mathcal{P}} g(\rho) \sum_n w_n \mu_n(d\rho) = \\ &= \sum_n w_n \int_{\mathcal{P}} g(\rho) \mu_n(d\rho) = \sum_n w_n \langle \bar{g} \rangle_n. \end{aligned} \quad (4.5)$$

Among the measures that can be defined on \mathcal{P} are the *Dirac measures* defined as follows. Let ρ_o be a state operator and let E be any subset of \mathcal{P} . The corresponding Dirac measure μ_{ρ_o} is (cf. G. Fano (1971), p.207)

$$\mu_{\rho_o}(E) = \begin{cases} 1 & \text{if } \rho_o \in E \\ 0 & \text{if } \rho_o \notin E \end{cases}. \quad (4.6)$$

The Dirac measures are *irreducible* into weighted sums of *different* measures, since their *support* (intended here as that part of the domain \mathcal{P} for which the measure is nonzero) is indivisible, being a *single point* in the phase-domain: the state operator ρ_o .

Since to every homogeneous preparation (i.e., to every state operator ρ) there corresponds a Dirac measure, and the Dirac measures are irreducible, it follows that condition (ii) of Section 3.2.3 is satisfied.

Condition (iii) is also satisfied. In fact, the following theorem holds:

every normalized measure μ defined on the domain \mathcal{P} can be *uniquely* decomposed into a “weighted sum” of Dirac measures.

To prove this theorem we write the generic measure μ as a “weighted sum” of Dirac measures

$$\mu = \int_{\mathcal{P}} \mu_{\rho} \sigma(d\rho). \quad (4.7)$$

where σ is some measure expressing the weight with which each component Dirac measure μ_{ρ} participates to form the measure μ . From the definition of Dirac measures, it is easy to see that $\sigma = \mu$, a *unique* solution. In fact, for any subset E of \mathcal{P} , equation 4.7 becomes

$$\mu(E) = \int_E \sigma(d\rho) = \sigma(E). \quad (4.8)$$

In other words, the generic measure μ represents the weight with which each Dirac measure participates to form the measure μ itself. This theorem also implies that the Dirac measures are the only irreducible measures definable over \mathcal{P} . In fact, any other measure can be decomposed into a “sum” of Dirac measures and is therefore reducible. The physical meaning of this theorem is that the descriptor of a generic preparation, i.e. the generic measure μ , admits of a *unique “spectral” resolution* into the descriptors of its homogeneous component preparations, i.e. the Dirac measures μ_{ρ} .

We conclude that the mathematical description of a heterogeneous preparation by means of a measure μ defined on the quantal phase-domain is adequate, unambiguous and does not lead to paradoxes. We are finally in the position to propose the paradigm of Quantum Statistical Thermodynamics.

4.2.2 The Paradigm of Quantum Statistical Thermodynamics

The paradigm of Quantum Statistical Thermodynamics is based on the following five postulates.

P1QST: Systems

Same as P1QT (Section 4.1.1).

Definition: Quantal Phase-domain

Same as in Section 4.1.1.

P2QST: Preparations

To every *preparation* scheme Π for a system, there corresponds a *measure* μ defined on the quantal phase-domain \mathcal{P} of the system, satisfying the normalization condition

$$\mu(\mathcal{P}) = \int_{\mathcal{P}} \mu(d\rho) = 1. \quad (4.2)$$

We call μ the *statistical-weight measure*.

P3QST: Physical Observables

Some real functionals g, h, \dots defined on \mathcal{P} correspond to *physical observables* of the system. Given an ensemble of identical systems prepared according to the scheme Π , with associated statistical-weight measure μ , the *expected mean value* $\langle \bar{g} \rangle$ of measurements of the observable g is given by

$$\langle \bar{g} \rangle = \int_{\mathcal{P}} g(\rho) \mu(d\rho). \quad (4.3)$$

P4QST: States

Same as P4QT. I.e., every system is always in a *state* described by some *state operator* ρ in the corresponding quantal phase-domain.

P5QST: Causal Evolution

Same as P5QT. The corresponding evolution of the statistical-weight measure is given by the equation

$$\frac{d\mu}{dt} = \int_{\mathcal{P}} \frac{d\mu_{\rho}}{dt} \mu(d\rho) \quad (4.9)$$

where

$$\frac{d\mu_{\rho}}{dt} = \lim_{dt \rightarrow 0} \frac{\mu_{\rho} + \hat{N}(\rho)dt - \mu_{\rho}}{dt} \quad (4.10)$$

expresses the evolution of the Dirac measures under the motion generated by the superoperator \hat{N} .

The solution of the limit defining the evolution of a Dirac measure (eq. 4.10) in terms of the evolution superoperator \hat{N} as given in Chapter 5 (eq. 5.30) is an interesting unsolved problem. Another interesting open problem is a complete mathematical characterization of the measure-theoretic properties of the quantal phase-domain. For example, it would be important to establish whether a Lebesgue measure can be defined over the quantal phase-domain. This measure might be the descriptor associated with the “most” heterogeneous preparation, obtained by uniform composition of all the possible homogeneous preparations for a system.

The following theorems of Quantum Statistical Thermodynamics summarize the results of the last Section, where we already concluded that the description of preparations by means of a statistical-weight measure is unambiguous.

Th1QST

Among the normalized measures definable on the phase-domain \mathcal{P} , only the Dirac measures μ_{ρ} are *irreducible*, in the sense that the equality

$$\mu_{\rho} = w_1 \mu_1 + w_2 \mu_2 \quad \text{with} \quad w_1, w_2 > 0 \quad (4.11)$$

holds if, and only if, $\mu_1 = \mu_2 = \mu_{\rho}$.

Th2QST

To every distinct state operator ρ in \mathcal{P} there corresponds a distinct Dirac measure μ_ρ defined on \mathcal{P} .

Definition: Homogeneous preparations within QST

A preparation is said to be homogeneous if, and only if, it is described by a Dirac measure.

Th3QST

Among all the preparation schemes for a physical system, only the *homogeneous* preparations cannot be conceived as the result of a statistical composition of *different* preparation schemes. Moreover, each homogeneous preparation corresponds to one and only one *state* of an individual system, and vice versa.

Th4QST

Every normalized measure μ defined on \mathcal{P} can be uniquely expressed as a “weighted sum” of Dirac measures, i.e.

$$\mu = \int_{\mathcal{P}} \mu_\rho \sigma(d\rho) . \quad (4.7)$$

where the measure μ itself represents the “weight” of the corresponding Dirac measure. Consequently, every heterogeneous preparation can be *uniquely resolved* into its homogeneous component preparations.

4.2.3 Empirical Determination of the Statistical-weight Measure

A measure μ defined on the quantal phase-domain \mathcal{P} can be “represented” as follows. Let \mathcal{L} be the real space of linear, Hermitian operators on the Hilbert space of the system. Let the scalar product $(\ , \)$ in \mathcal{L} be defined by the trace formula

$$(F, G) = \text{Tr}(FG) . \quad (4.12)$$

Two operators in \mathcal{L} are said to be orthogonal if their scalar product vanishes. Let the operators Q_i and R_j form two bases for \mathcal{L} satisfying the following orthonormalization conditions:

$$\text{Tr}(Q_i Q_n) = \delta_{in} \quad \text{Tr}(R_j R_m) = \delta_{jm} . \quad (4.13)$$

The state operators are elements of the domain \mathcal{P} which is a convex subset of \mathcal{L} and may therefore be expanded in terms of such bases:

$$\rho = \sum_i q_i Q_i = \sum_j r_j R_j \quad (4.14a)$$

where

$$q_i = \text{Tr}(\rho Q_i) \quad r_j = \text{Tr}(\rho R_j) . \quad (4.14b)$$

As discussed by W. Band and J.L. Park (1977a), once a basis is specified, the “coordinates” q_i (or r_j) of any state operator identify a point in an auxiliary real space. As the state operator sweeps the quantal phase-domain, the point in the auxiliary space sweeps a convex region \mathcal{D}_Q (or \mathcal{D}_R).

Once the domain \mathcal{P} has been coordinatized, any functional $g(\rho)$ defined on it can be written as a function of the corresponding coordinates $g_Q(\underline{q})$ (or $g_R(\underline{r})$) defined on the corresponding region of the auxiliary real space. Moreover, any measure μ defined on \mathcal{P} can generally be written as follows

$$\mu(d\rho) = w_Q(\underline{q})d\underline{q} = w_R(\underline{r})d\underline{r} \quad (4.15)$$

where the functions w_Q or w_R “represent” the measure with respect to the corresponding coordinatization of the phase-domain. Accordingly, the expected mean value of a physical observable represented by the functional g is given by

$$\langle \bar{g} \rangle = \int_{\mathcal{P}} g(\rho) \mu(d\rho) = \int_{\mathcal{D}_Q} g_Q(\underline{q}) w_Q(\underline{q}) d\underline{q} = \int_{\mathcal{D}_R} g_R(\underline{r}) w_R(\underline{r}) d\underline{r}. \quad (4.16)$$

In view of this background, we can now pose the following question: Is it possible to identify a list, or “quorum”, of independent physical observables such that the empirical determination of their expected mean values is tantamount to the empirical determination of the statistical-weight measure μ ? This question is composed of two equally important subproblems. The first subproblem is mathematical and it is to determine whether there exists a set of functionals $g_i(\rho)$ (not necessarily linear) on \mathcal{P} such that the system of equations

$$\int_{\mathcal{P}} g_i(\rho) \mu(d\rho) = \langle \bar{g}_i \rangle \quad (4.17)$$

can be “solved” for the unknown μ , once all the $\langle \bar{g}_i \rangle$ ’s are given. The second subproblem is to identify the physical meaning of such functionals.

We have not solved these two problems. However, for the first subproblem we can suggest two interesting “moment” generating functions which might prove to be sufficient for the empirical determination of the statistical-weight measure. The first generating function is

$$f(u) = \int_{\mathcal{P}} \text{Tr}(\exp(ug(\rho))) \mu(d\rho) \quad (4.18)$$

where u may be a complex variable. If the function $f(u)$ had been empirically determined, then the following sequence of mean values would be known

$$\left. \frac{\partial^n f}{\partial u^n} \right|_{u=0} = \int_{\mathcal{P}} \text{Tr}(\rho^n) \mu(d\rho). \quad (4.19)$$

The second generating function is

$$g'(u) = \int_{\mathcal{P}} \exp(ug(\rho)) \mu(d\rho) \quad (4.20)$$

where g may be any functional on \mathcal{P} . If $g'(u)$ were known, then the following sequence of mean values would be known

$$\left. \frac{\partial^n g'}{\partial u^n} \right|_{u=0} = \int_{\mathcal{P}} g^n(\rho) \mu(d\rho). \quad (4.21)$$

It remains to be proved that the empirical determination of one of these generating functions or of a sequence of them is mathematically equivalent to the empirical determination of the measure μ .

4.2.4 Quantum Statistical Thermodynamics and Information Theory

In this Section, we consider three problems pertaining to the domain of Information Theory. Here, these problems acquire physical significance within Quantum Statistical Thermodynamics. However, their conceptual nature is independent of the formulation of QST and it has been widely discussed in the literature, with or without reference to other statistical theories (e.g., cf. R.D. Levine and M. Tribus (1978) and, for a recent mathematical treatment, N.F.G. Martin and J.W. England (1981); it is to be noticed that, in this literature, the terms “informational entropy” or, simply, “entropy” refer to what we shall call *statistical uncertainty*, in order to avoid confusion between those information-theoretic concepts and the quantum thermodynamical observable entropy of any individual physical system).

The three problems are about an experimenter or “observer” accepting for study *individual* systems prepared according to a heterogeneous preparation scheme. They are:

- (a) The observer knows the statistical-weight measure corresponding to the preparation (e.g., he has determined it by previous experiments). Therefore, he knows completely the statistical structure of the heterogeneous preparation, since, by analysis of the statistical-weight measure, he can identify the component homogeneous preparations and their statistical weights. However, he cannot predict according to which of the component homogeneous schemes the next single system is going to be actually prepared. The first information-theoretic problem is to define an *indicator* of the uncertainty of the observer about the outcome of the next single act of preparation. In other words, this indicator should globally quantify the heterogeneity of the preparation scheme. This problem is conceptually identical to that considered by C.E. Shannon (1948) in his famous article.
- (b) The observer does not know the statistical-weight measure of the preparation, however, he knows which are its component homogeneous preparations (i.e., by some means he has determined the “spectrum” of the statistical-weight measure). In addition, he also knows the expected values of a limited number of physical observables. The second information-theoretic problem is to find the most probable statistical-weight measure consistent with the given expected mean values and the additional available information about the component homogeneous preparations.
- (c) The observer does not know the statistical-weight measure of the preparation. All he knows are the expected mean values of a limited number of physical observables. The third information-theoretic problem is also to find the most probable statistical-weight measure consistent with the given expected mean values. Differently from the previous problem, here the spectrum of the statistical-weight measure is also an unknown. The last two problem are conceptually identical to those considered by E.T. Jaynes (1957) in his famous and subsequent articles.

Problem (a) can be solved by defining an indicator I_μ of the heterogeneity of a preparation scheme described by the statistical-weight measure μ . The indicator I_μ must globally quantify an objective characteristic – the heterogeneity – of the preparation. Since this characteristic is

already contained in the statistical-weight measure, the indicator should be defined in terms of the properties of such measure only. If the resolution of μ into Dirac measures identifies a countable spectrum, i.e.

$$\mu = \sum_n w_n \mu_{\rho_n}, \quad (4.4)$$

then, by analogy with Shannon's problem (cf. eq. 2.1), we can define

$$I_\mu = -c \sum_n w_n \ln w_n. \quad (4.22a)$$

It is noteworthy that $0 \leq I_\mu \leq c \ln N$, where N is the number of points forming the spectrum of the measure and may be finite or infinite. If the spectrum is instead not countable, then it is possible to define (as we will see for problem (c)) indicators that are relative to some *a priori* partition of the quantal phase-domain. However, such definitions are not suitable to solve the present problem, because *a priori* partitions are not inherent characteristics of the measure μ . Instead, if the spectrum is not countable, we set

$$I_\mu = \infty \quad (4.22b)$$

and justify this definition arguing that in this case the heterogeneity is greater than any of the cases with countable resolution, thus including those with $I_\mu = c \ln N$ and $N = \infty$.

We call the indicator I_μ the *statistical uncertainty* associated with the preparation scheme described by μ . This definition is of key importance to approach problems (b) and (c). In fact, essential to their solution is Jaynes' *maximum statistical uncertainty principle*. As we have seen in Chapter 2, this principle is known as the *maximum "entropy" principle*, however, the term entropy has already been used in Quantum Thermodynamics to indicate an important physical observable of any material system. Thus, we shall not use it to indicate also the present information-theoretic concept. This principle, in our case, prescribes that, among the statistical-weight measures sharing the known expected mean values and the remaining known characteristics, the most probable measure is that with the maximum value of the indicator of statistical uncertainty, i.e. the most heterogeneous.

Problem (b) can be readily solved by means of Jaynes' principle when the known set of component homogeneous preparations is countable (i.e., the spectrum of the statistical-weight measure is countable). Assume, for example, that the only known expected mean value is that of the energy. Then, the most probable statistical-weight measure is to be found by maximizing

$$I_\mu = -c \sum_n w_n \ln w_n$$

subject to the constraint

$$\langle \bar{h} \rangle = \int_{\mathcal{P}} h(\rho) \mu(d\rho) = \sum_n w_n \langle \bar{h} \rangle_n \quad (4.23)$$

where $\langle \bar{h} \rangle$ is known (presumably, as a result of previous experiments) and

$$\langle \bar{h} \rangle_n = \text{Tr}(H \rho_n) \quad (4.24)$$

are also known, since the spectrum of the measure is known and so are therefore the corresponding state operators ρ_n . Maximization yields the following most probable statistical-weight measure

$$\mu = \sum_n q_n \mu_{\rho_n} \quad (4.25)$$

where

$$q_n = \frac{\exp(-b\langle \bar{h} \rangle_n)}{\sum_m \exp(-b\langle \bar{h} \rangle_m)} \quad (4.26)$$

and the parameter b is fixed by the given expected mean value of the energy. When the spectrum of the statistical-weight measure is known but not countable, the solution involves difficulties as discussed below for problem (c).

Problem (c) can also be given a solution which is not, however, fully satisfactory. This solution is based on a different definition of statistical uncertainty for the case in which the spectrum of the statistical-weight measure is, a priori, the whole quantal phase-domain (or some known region of it, for problem (b)). An important, and somewhat unsatisfactory, feature of the following definition is that it depends not only on the statistical-weight measure but also on an *a priori* selected countable partition of the quantal phase-domain. Let the collection of disjoint subsets E_n form a particular countable partition ζ of the quantal phase-domain \mathcal{P} . With respect to this partition, the following definition of statistical uncertainty can be given

$$I_\mu(\zeta) = -c \sum_n \mu(E_n) \ln \mu(E_n). \quad (4.27)$$

Maximization of this indicator, subject to the constraints expressing the known expected mean values, yields the most probable statistical-weight measure relative to partition ζ . Again, if the only expected mean value is the energy, we write

$$\langle \bar{h} \rangle = \int_{\mathcal{P}} h(\rho) \mu(d\rho) = \sum_n \int_{E_n} h(\rho) \mu(d\rho) = \sum_n \mu(E_n) \langle \bar{h}(E_n) \rangle \quad (4.28)$$

where the last equality defines the expected mean energy $\langle \bar{h}(E_n) \rangle$ within the n -th cell of the partition. Maximization in this case yields

$$\mu(E_n) = \frac{\exp(-b\langle \bar{h}(E_n) \rangle)}{\sum_m \exp(-b\langle \bar{h}(E_m) \rangle)}. \quad (4.29)$$

This expression does not identify a single most probable statistical-weight measure but a family of measures sharing these values on the subsets E_n . A more unsatisfactory aspect of this solution is its dependence on the choice of the a priori partition of phase-domain. Different a priori partitions would yield different solutions. Since, by the definition of the problem, no information is available about the structure of the preparation and therefore on the statistical-weight measure, we need an additional criterion (perhaps based on the nature of the constraints or on the type of estimates that one plans to make with the result) to choose among different partitions of quantal phase-domain. Presumably, this as yet unknown criterion is to be postulated independently of, and in addition to, the maximum statistical uncertainty principle.

The following example sharpens the distinction between the physical observable entropy and the information-theoretic indicator of statistical uncertainty.

4.2.5 Example. Entropy vs Statistical Uncertainty

Let Π_1 and Π_2 be two distinct homogeneous preparations for a given system. We want to describe the heterogeneous preparation corresponding to the symbolic expression (cf. Section 3.1.2)

$$\Pi = w_1 \Pi_1 + w_2 \Pi_2 \quad \text{with} \quad w_1 + w_2 = 1 \text{ and } w_1, w_2 > 0.$$

According to the paradigm of Quantum Thermodynamics, the two homogeneous preparations are described by the state operators ρ_1 and ρ_2 , respectively. We now define the measure μ corresponding to the heterogeneous preparation Π . Let E be any subset of the quantal phase-domain \mathcal{P} of the system. Then

$$\mu(E) = \begin{cases} w_1 & \text{if } \rho_1 \in E \text{ and } \rho_2 \notin E \\ w_2 & \text{if } \rho_1 \notin E \text{ and } \rho_2 \in E \\ 1 & \text{if } \rho_1 \in E \text{ and } \rho_2 \in E \\ 0 & \text{if } \rho_1 \notin E \text{ and } \rho_2 \notin E \end{cases} . \quad (4.30)$$

It is easy to check that μ is a measure defined on \mathcal{P} and that the normalization condition $\mu(\mathcal{P}) = 1$ is satisfied.

From the definition of μ , it is immediately seen that

$$\mu = w_1 \mu_{\rho_1} + w_2 \mu_{\rho_2} . \quad (4.31)$$

This represents the spectral resolution of μ into its component Dirac measures. Interestingly, the expected mean value of the physical observable *entropy*, represented by the functional $s(\rho) = -k \text{Tr}(\rho \ln \rho)$, is given by

$$\begin{aligned} \langle \bar{s} \rangle &= -k \int_{\mathcal{P}} \text{Tr}(\rho \ln \rho) \mu(d\rho) = \\ &= -kw_1 \text{Tr}(\rho_1 \ln \rho_1) - kw_2 \text{Tr}(\rho_2 \ln \rho_2) = w_1 \bar{s}_1 + w_2 \bar{s}_2 . \end{aligned} \quad (4.32)$$

It is important to note that this expression is unequivocally different from the value of the indicator of *statistical uncertainty* for the same heterogeneous preparation. In fact, the corresponding expression for I_μ is

$$I_\mu = -c(w_1 \ln w_1 + w_2 \ln w_2) . \quad (4.33)$$

As explained above, this quantity is an index of the heterogeneity of the preparation scheme and is totally independent of the physical nature of the states of systems prepared according to such scheme, i.e. of the nature of the component homogeneous preparations. In fact, equation 4.33 is totally independent of the state operators ρ_1 and ρ_2 .

Chapter 5

NEW GENERAL QUANTUM THEORY: DYNAMICS

This Chapter completes the dynamical postulate P5QT of Quantum Thermodynamics by proposing a general expression for the evolution superoperator \hat{N} . The new law of causal evolution has been conceived so as to entail both a statement of the second law of Thermodynamics and a statement of existence of irreversible processes. Conversely, these two statements emerge from Quantum Thermodynamics as manifestations of the fundamental quantum dynamical behaviour of the elementary constituents of any individual material system.

An introductory discussion and some necessary preliminary definitions are presented in Section 5.1. The equation of motion is proposed in Section 5.2.

5.1 GENERAL REMARKS AND DEFINITIONS

According to postulate P5QT, the general law of causal evolution of Quantum Thermodynamics has of the form

$$\frac{d\rho}{dt} = \hat{N}(\rho) \quad (4.1)$$

where \hat{N} is the evolution superoperator of the system and ρ is the state operator. Before introducing the explicit form of the evolution superoperator \hat{N} , we examine the motivations for developing a new nonlinear irreversible quantum dynamics.

5.1.1 Incompleteness of Hamiltonian Dynamics

As shown by F. Strocchi (1966), the Schrödinger equation of motion (eq. 3.8) can be viewed as a natural extension to Quantum Mechanics of the Hamilton equations of motion of Classical Mechanics (eq. 3.1). As we have noticed in Section 4.1.1, in Quantum Thermodynamics the states of Quantum Mechanics are described by a particular subset of state operators, namely, the projection operators P_ψ onto one-dimensional subspaces of the Hilbert space spanned by the vectors ψ (the state vectors of Quantum Mechanics). As the state vector evolves according to the Schrödinger equation, the corresponding projection operator evolves according to the equation

$$\frac{dP_\psi}{dt} = -\frac{i}{\hbar}[H, P_\psi] \quad (5.1)$$

where H is the Hamiltonian operator of the system. The extension of equation 5.1 to describe the evolution of any state operator of Quantum Thermodynamics, i.e.

$$\frac{d\rho}{dt} = -\frac{i}{\hbar}[H, \rho], \quad (5.2)$$

will be said to describe the Hamiltonian evolution of the state operator. The corresponding evolution superoperator is the so-called *Liouvillian superoperator*

$$\hat{L}_o(\rho) = -\frac{i}{\hbar}[H, \rho]. \quad (5.3)$$

A mathematically identical equation was obtained by J. von Neumann (1932) for the statistical operator W of Quantum Statistical Mechanics (eq. 3.12). However, the physical significance of the von Neumann equation is completely different from equation 5.3, due to the essential difference between a state operator ρ and a statistical operator W (cf. Section 4.1.1).

A process of an *isolated system* (the object of study of Quantum Thermodynamics) is said to be reversible (irreversible) if the mean value of the entropy during the process remains constant (increases). The incompleteness of Hamiltonian dynamics regards both the notion of *irreversibility* and that of *reversibility*. It stems from the following reasoning:

- (a) A theorem of the Hamiltonian evolution generated by the Liouvillian superoperator is: the mean value of the entropy is a constant of the motion for an isolated system. According to Quantum Thermodynamics, entropy is a physical property of matter. Therefore, if irreversibility exists, then it must be a fundamental physical phenomenon since, by definition, it must entail an increase in the physical property entropy. Common experience shows that most physical processes of isolated systems are irreversible. Therefore, entropy cannot be a constant of the motion for isolated systems. Hence, Hamiltonian dynamics is incompatible with irreversible physical reality.
- (b) The entropy functional can be written as follows

$$s(\rho) = -k\text{Tr}(\rho \ln \rho) = -k \sum_i p_i \ln p_i \quad (5.4)$$

where p_i is the i -th eigenvalue of the state operator ρ and the sum runs over a complete set of eigenvectors of ρ . A theorem of the Hamiltonian evolution generated by the Liouvillian superoperator is: each eigenvalue p_i of the state operator is a constant of the motion for an isolated system. Such a theorem implies that the entropy remains constant in a very special way (Hamiltonian reversibility) and that there could not exist reversible processes in which the entropy remains constant while the eigenvalues p_i vary. However, as shown by Hatsopoulos and Gyftopoulos (1976), there exist examples of important reversible processes of this type. Hence, Hamiltonian dynamics is incomplete even as regards the notion of reversibility.

These two considerations motivate the search for a more general equation of motion for Quantum Thermodynamics.

5.1.2 Inadequacy of Generalized Linear Dynamics

In the search for a more general equation of motion, a logical approach is to consider *linear* evolution superoperators that generalize the Liouvillian superoperator (cf. J.L. Park and W. Band (1977b)). In appendix B (eq. B.2) we consider the explicit form of the most general linear evolution superoperator \hat{L} that could be postulated to generate the motion of the state operator via the following equation

$$\frac{d\rho}{dt} = \hat{L}(\rho). \quad (5.5)$$

We take the position that such generalized linear equation of motion is inadequate for the purposes of Quantum Thermodynamics. The inadequacy regards the notions of natural tendency towards a stable equilibrium state and of rate of entropy production. It stems from the following reasoning:

- (a) It is thermodynamically legitimate, though not strictly necessary, to require that the general equation of motion eventually transform any initial state of an isolated system into the corresponding stable equilibrium state with the same mean values for the energy and the other constants of the motion. This feature would represent a genuine natural tendency towards a stable equilibrium state. However, R.S. Simmons (1979) has proved that, for a system whose Hilbert space is more than two-dimensional, there exist *no* linear equations of motion capable of eventually transforming *all* given initial state operators into the corresponding stable equilibrium state operators. Hence, the notion of natural tendency towards stable equilibrium states cannot be described by a linear equation of motion.
- (b) In appendix B we give an expression (eq. B.7a) for the rate of entropy production implied by the explicit form of the most general linear evolution superoperator \hat{L} . It follows from such expression that if the state operator is singular (i.e., at least one of its eigenvalues is zero), then the rate of entropy production can generally be *infinite*. This practically unknown characteristic feature of linear dynamics is not, strictly, in conflict with the laws of either Mechanics or Thermodynamics. However, it implies that a large class of states (including all the states contemplated in Quantum Mechanics) are highly unstable and tend towards more stable states at an infinite rate.

These considerations led us to consider *nonlinear* evolution superoperators.

5.1.3 Constitutive Structure of a Physical System

We will see that the evolution superoperator \hat{N} (eq. 5.30) is strongly nonlinear in the state operator and its form depends explicitly on the structure of the system. For example, the form of \hat{N} for a single structureless electron differs substantially from the form of \hat{N} for a single electron with internal structure. Thus, according to the proposed nonlinear dynamics, these systems must be considered as two *essentially* different physical systems.

Given any physical system, it is necessary to specify exactly its *constitutive structure* in order to write the corresponding evolution superoperator. The constitutive structure of a system is defined here as the list of its *elementary constituents*.

The term *elementary constituent* of a material system is taken to be a *primitive concept* of the present theory, analogous to the concept of “particle” in Newtonian mechanics. What is judged elementary in physics is of course subject to sometimes rapid historical evolution; thus the actual admissible referents of the term elementary constituent should be left unspecified in the present general discussion. However, to fix the ideas, we give the following examples of elementary constituents: a single fermion (electron, nucleon, ...) or boson (photon, meson, ...), a fermion or boson field (e.g., the electromagnetic field).

To every system composed of a single elementary constituent, according to postulate P1QT of Quantum Thermodynamics, there corresponds a Hilbert space. The Hilbert space corresponding to a general composite system, i.e. a composite of M distinguishable elementary constituents, is

$$\mathcal{H} = \bigotimes_{J=1}^M \mathcal{H}(J) = \mathcal{H}(1) \otimes \mathcal{H}(2) \otimes \cdots \otimes \mathcal{H}(M) \quad (5.6)$$

where $\mathcal{H}(J)$ is the “factor” Hilbert space corresponding to the J -th elementary constituent. We will see that, in the framework of Quantum Thermodynamics, this “factorization” of the Hilbert space \mathcal{H} acquires an important dynamical significance, since the structure of the evolution superoperator depends explicitly on it.

Mathematically, any given Hilbert space can be factored in many different ways. Within Hamiltonian dynamics these different factorizations do not play any role and, therefore, are all equivalent. However, within the present nonlinear dynamics, different factorizations correspond to different physical systems, since they yield different equations of motion. Therefore, it is essential that the proper selection of the elementary constituents be made.

5.1.4 Generators of the Motion

In conventional quantum dynamics, the term *generator of the motion* is synonymous with the Hamiltonian. Here, however, we extend this notion to refer to members of a set of operators which enter explicitly into the dynamical law and in that sense determine, or “generate”, the motion.

We postulate that to every type of elementary constituent there corresponds a list of operators (the *generators of the motion*)

$$H, X, \dots, Y$$

defined on the Hilbert space of a system composed of the elementary constituent only. We further postulate that the first generator of the list is always the standard Hamiltonian operator H associated with the elementary constituent, and that the remaining generators X, \dots, Y are *dimensionless* Hermitian operators all commuting with H . We call them the *non-Hamiltonian generators* of the elementary constituent. For generality, their number and physical significance will be left unspecified, since they depend on the particular type of elementary constituent under consideration. However, we will see that a theorem of the new dynamics is that the generators of the motion, together with the identity operator, form a complete set of constants of the motion for the elementary constituent. This result should be used to identify the non-Hamiltonian generators associated with different elementary constituents. For example, candidates for this role are: the number of particles operator (if the elementary constituent is a field), the angular momentum operator, the momentum operator, etc. Identification of the non-Hamiltonian generators associated with the known elementary constituents of matter has not been attempted in this work and is an open avenue for further theoretical and experimental investigation.

5.1.5 Separable Systems and Independent States

We have said that the object of study of Quantum Thermodynamics is any *isolated* physical system. In fact, the equation of motion of Quantum Thermodynamics, as proposed in the next Sections, applies only to isolated systems. Here, we give an explicit definition of the term isolated system, together with some preliminary definitions and corollaries of Quantum Thermodynamics that are independent of the dynamical postulate and will serve in the definition of the evolution superoperator for a general composite system.

Let us consider a general composite system as defined in Section 5.1.3. The index J identifies the elementary constituents of the system and runs over the set of labels 1, 2, ..., M . The Hilbert space of such a system is

$$\mathcal{H} = \bigotimes_{J=1}^M \mathcal{H}(J). \quad (5.6)$$

Let us consider a partition of the composite system into subsystems. The elementary constituents are grouped into disjoint subsets forming the subsystems. Correspondingly, the set of labels 1, 2, ..., M is partitioned into disjoint subsets (e.g., (1, 3), (6, 5, 2), ..., (8, M)) which we index by the letter K . The index $J(K)$ will identify the J -th elementary constituent of the K -th subsystem and run over the set 1, 2, ..., $M(K)$, where $M(K)$ is the total number of elementary constituents of subsystem K . The Hilbert space corresponding to subsystem K is

$$\mathcal{H}(K) = \bigotimes_{J(K)=1}^{M(K)} \mathcal{H}(J(K)). \quad (5.7)$$

An apostrophe following an index shall identify the “complementary” of what is otherwise identified by the index. For example, J' identifies the subsystem of the composite system formed by all the elementary constituents except the J -th one; K' the subsystem of the composite system formed by all the subsystems except the K -th one; $J'(K)$ all the elementary constituents of subsystem K except the $J(K)$ -th one; $J(K)'$ the subsystem of the composite system formed by all the elementary constituents except the $J(K)$ -th one; finally, $J(K')$ the J -th elementary constituent of subsystem K' .

Definition: Separable Subsystems

A subsystem K of a composite system is said to be *separable* if, and only if, the Hamiltonian operator of the composite system can be written as

$$H = H(K) \otimes I(K') + I(K) \otimes H(K') \quad (5.8)$$

where $H(K)$ is the Hamiltonian operator on $\mathcal{H}(K)$ corresponding to a system composed of subsystem K only. The operator $H(K)$ can be called the *private* Hamiltonian operator of the K -th subsystem.

Definition: Separable Systems

A system is said to be *separable* if, and only if, it is a separable subsystem of every conceivable composite system which contains it.

Corollary: Additivity of Energy for Separable Subsystems

The mean value of the energy for a system composed of two *separable* subsystems K and K' is equal to the sum of the “private energy” values for two subsystems, i.e.

$$\begin{aligned}\bar{h} &= \text{Tr}_{\mathcal{H}}(H\rho) = \text{Tr}_{\mathcal{H}(K)}(H(K)\rho(K)) + \text{Tr}_{\mathcal{H}(K')}(H(K')\rho(K')) = \\ &= \bar{h}(K) + \bar{h}(K').\end{aligned}\tag{5.9}$$

Definition: Reduced State Operator of a Subsystem

Let ρ be the state operator of a composite system. The operator

$$\rho(K) = \text{Tr}_{\mathcal{H}(K')}(\rho)\tag{5.10}$$

defined on the corresponding Hilbert space $\mathcal{H}(K)$ is called the *reduced state operator* of subsystem K .

Definition: Independent State of a Subsystem

A subsystem K of a composite system is said to be in an *independent state* if, and only if, the state operator ρ of the composite system can be written as

$$\rho = \rho(K) \otimes \rho(K')\tag{5.11}$$

where $\rho(K)$ is the reduced state operator of subsystem K and $\rho(K')$ is the reduced density operator of the “complementary” subsystem K' . Only in this case, the following relation holds

$$\ln \rho = \ln \rho(K) \otimes I(K') + I(K) \otimes \ln \rho(K').\tag{5.12}$$

Definition: Independent Systems

A system is said to be *independent* if, and only if, it is a subsystem in an independent state of every conceivable composite system which contains it.

Corollary: Additivity of Entropy for Subsystems in Independent States

The mean value of the entropy for a system composed of two subsystems K and K' in *independent states* is equal to the sum of the “private entropy” values for the two subsystems, i.e.

$$\begin{aligned}\bar{s} &= -k\text{Tr}_{\mathcal{H}}(\rho \ln \rho) = -k\text{Tr}_{\mathcal{H}(K)}(\rho(K) \ln \rho(K)) - k\text{Tr}_{\mathcal{H}(K')}(\rho(K') \ln \rho(K')) = \\ &= \bar{s}(K) + \bar{s}(K').\end{aligned}\tag{5.13}$$

In general (cf. E.H. Lieb and M.B. Ruskai (1973)), the following inequality holds

$$\bar{s} \leq \bar{s}(K) + \bar{s}(K')\tag{5.14}$$

where the equal sign holds if, and only if, subsystem K is in an independent state (this property of the entropy is called *subadditivity*).

Definition: Isolated Systems

A system is said to be isolated if, and only if, it is separable and independent.

Since, as we will see, a separable system which is initially independent remains independent indefinitely, this definition implies that an isolated system must be independent at the moment of its “creation”.

5.2 NEW EQUATION OF MOTION FOR GENERAL QUANTUM DYNAMICS

In view of the foregoing discussion and definitions we can now present the equation of motion that we propose for Quantum Thermodynamics. The equation of motion is introduced first for the particular case of a system composed of a single elementary constituent (eq. 5.16) and then for the case of a general composite system (eq. 5.30).

5.2.1 Equation of Motion for a Single Elementary Constituent

Let the system of interest consist of only one elementary constituent. The corresponding Hilbert space is \mathcal{H} . We have postulated that the corresponding list of generators of the motion is

$$H, X, \dots, Y \quad (5.15)$$

where we recall that the dimensionless generators X, \dots, Y , commute individually with the Hamiltonian operator H . We further postulate that to every type of elementary constituent there corresponds a positive time constant τ entering explicitly its dynamical law of causal evolution.

The proposed equation of motion for a single elementary constituent is

$$\frac{d\rho}{dt} = -\frac{i}{\hbar}[H, \rho] - \frac{\tau}{\hbar^2}\{D, \rho\} \quad (5.16)$$

where $\{, \}$ is the anticommutator symbol ($F, G = FG + GF$), D is an operator on \mathcal{H} defined by the determinant

$$D = \begin{vmatrix} \Delta(\ln \rho) & \Delta H & \Delta X & \dots & \Delta Y \\ (H, \ln \rho) & (H, H) & (H, X) & \dots & (H, Y) \\ (X, \ln \rho) & (X, H) & (X, X) & \dots & (X, Y) \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ (Y, \ln \rho) & (Y, H) & (Y, X) & \dots & (Y, Y) \end{vmatrix}, \quad (5.17)$$

and the symbols ΔF and (F, G) , for F and G any Hermitian operator, are defined by

$$\Delta F = F - I \text{Tr}(\rho F) \quad (5.18)$$

and

$$(F, G) = \text{Tr}(\rho\{\Delta F, \Delta G\}). \quad (5.19)$$

Note that $(F, G) = (G, F)$ is a scalar product on the real space \mathcal{L} of linear, Hermitian operators on \mathcal{H} . As we will see in the next Section, the proposed equation of motion 5.16 entails the Schrödinger equation as a particular case, implies the existence of irreversible processes for a single elementary constituent, yields an explicit expression for the rate of entropy production and entails a generalized statement of the second law of Thermodynamics.

The experimental verification of the proposed equation of motion for a single elementary constituent is clearly an open problem of fundamental theoretical and practical importance. Moreover, the identification of the non-Hamiltonian generators of the motion and the time constant that are associated with every elementary constituent, is still an open problem. However, the major theorems that follow are independent of the specific form and number of generators of the motion, and apply therefore to any elementary constituent of matter.

5.2.2 Theorems

The major theorems of the proposed dynamics of a single elementary constituent are as follows. Proofs are given in Appendix C.

Th1QT

If the state operator is a projection operator $\rho = P_\psi$, onto a one-dimensional subspace of \mathcal{H} , then the equation of motion 5.16 reduces to the Schrödinger equation and the evolution of the isolated single elementary constituent is therefore purely Hamiltonian.

Definition: Constants of the Motion

A physical observable c , represented by the functional $c(\rho)$ defined on the quantal phase-domain of the system, is said to be a *constant of the motion* if, and only if, the value of the representative functional is time invariant for any state of the system.

If the observable c is represented by a linear functional, then there exists a unique operator C such that, for all state operators ρ , $c(\rho) = \text{Tr}(C\rho)$. In this case the observable is said to be a *linear constant of the motion* if, and only if,

$$d\bar{c}(\rho)/dt = \text{Tr}(C(d\rho/dt)) = 0 \quad (5.20)$$

for all state operators.

Th2QT

A physical observable represented by a linear functional c or, equivalently, by a linear Hermitian operator C , is a constant of the motion if, and only if, C is a linear combination of the generators of the motion and the identity operator, i.e. of I, H, X, \dots, Y .

According to purely Hamiltonian dynamics (eq. 5.2), any Hermitian operator which commutes with H represents a linear constant of the motion. Theorem Th2QT states that not every linear constant of the motion according to Hamiltonian dynamics is a constant of the motion according to Quantum Thermodynamics. This is an important novel feature of the proposed equation of motion.

Definition: Equilibrium States

A state operator is said to represent an *equilibrium state* if, and only if, $d\rho/dt = 0$.

Th3QT

The following conditions are necessary and sufficient for equilibrium:

- (a) the state operator ρ commutes with the Hamiltonian operator H ; and

- (b) the state operator ρ commutes with a linear combination of the generators of the motion

$$R = -\beta H + \chi X + \dots + vY \quad (5.21a)$$

and the i -th eigenvalue p_i of ρ is either

$$p_i = 0 \quad (5.21b)$$

or

$$p_i = (1/z) \exp(R_i) \quad (5.21c)$$

where

$$z = \sum_i \exp(R_i) \quad (5.21d)$$

and the index i runs over an eigenbasis shared by ρ and R , whose existence is ensured by the fact that the two operators commute. Notice that state operators that are projection operators P_ψ onto one-dimensional subspaces of \mathcal{H} satisfying condition (a), also satisfy condition (b), the eigenvalues being all zero except for a single one equal to unity.

Th4QT

The mean value of the entropy increases with time at a rate given by the relation

$$d\bar{s}/dt = k\tau g/\hbar^2 \geq 0 \quad (5.22)$$

where g is a positive semi-definite nonlinear functional defined by the following determinant

$$g = \begin{vmatrix} (\ln \rho, \ln \rho) & (\ln \rho, H) & (\ln \rho, X) & \dots & (\ln \rho, Y) \\ (H, \ln \rho) & (H, H) & (H, X) & \dots & (H, Y) \\ (X, \ln \rho) & (X, H) & (X, X) & \dots & (X, Y) \\ \dots & \dots & \dots & \dots & \dots \\ (Y, \ln \rho) & (Y, H) & (Y, X) & \dots & (Y, Y) \end{vmatrix}. \quad (5.23)$$

The rate of entropy production $d\bar{s}/dt$ for a single elementary constituent is zero if, and only if, the state is an equilibrium state.

This theorem is a statement of existence of irreversible processes of any isolated physical system composed of a single elementary constituent. Any system in any non-equilibrium state will tend towards an equilibrium state with the same mean values of the constants of the motion and a higher mean value of the entropy.

Definition: Stable Equilibrium States

An equilibrium state operator ρ is said to represent a *stable equilibrium state* if, and only if, there exist *no* other state operators with the same mean values of the constants of the motion and a higher mean value of the entropy.

Though we state it as a definition, we conjecture that this statement should follow as a theorem of the proposed dynamics and the mathematical definition of stability according to A.M. Liapunov (1892) (cf. Appendix C). The definition just given can be justified as follows. Consider an equilibrium state (as specified by Theorem Th3QT) and the “plane” in quantal phase-domain of state operators with the same values of the constants of the motion. If on this “plane” there exists a state operator with a higher entropy than the equilibrium state under consideration, then it is possible to find “neighbouring” states of the equilibrium state that are non-equilibrium and proceed according to Theorem Th4QT towards states of higher entropy. Such “neighbouring” states would leave the “neighbourhood” of the equilibrium state without ever being able to return to it, since the entropy cannot decrease. Such an equilibrium state can therefore be said to be unstable. An equilibrium state will be stable only if it has the maximum entropy among the states with the same mean values of the constants of the motion.

Th5QT

Among the states of a system with given mean values of the constants of the motion, one and only one is a stable equilibrium state.

This fundamental theorem is in fact a generalization of a known statement of the second law of thermodynamics (cf. J.H. Keenan, G.N. Hatsopoulos and E.P. Gyftopoulos (1972)). Consequences of this theorem are discussed in Section 5.2.4.

Th6QT

The explicit expression of the state operator for any elementary constituent in a stable equilibrium state is

$$\rho = (1/Z) \exp(-\beta H + \chi X + \dots + vY) \quad (5.24a)$$

where

$$Z = \text{Tr}(\exp(-\beta H + \chi X + \dots + vY)) \quad (5.24b)$$

and the coefficients β, χ, \dots, v are determined by the initial values of a complete and independent set of linear constants of the motion. The function Z can be called the generalized *partition function*.

Th7QT

The mean value of the entropy for an elementary constituent in a stable equilibrium state can be written in terms of the mean values of the generators of the motion and the partition function:

$$\bar{s} = k\beta\bar{h} - k\chi\bar{x} - \dots - kv\bar{y} + k \ln Z. \quad (5.25)$$

This relation can be called the generalized Gibbs equation for a single elementary constituent.

5.2.3 Equation of Motion for a General Composite System

Let us consider a general system composed of M distinguishable elementary constituents. The corresponding Hilbert space is “structured” as follows

$$\mathcal{H} = \bigotimes_{J=1}^M \mathcal{H}(J). \quad (5.6)$$

We postulate that the list of generators of the motion for the J -th elementary constituent is

$$V(J), X(J), \dots, Y(J) \quad (5.26)$$

where the dimensionless operators $X(J), \dots, Y(J)$ are the non-Hamiltonian generators of the motion corresponding to a system composed of the J -th elementary constituent only. The operators $V(J)$ are defined instead as follows

$$V(J) = \text{Tr}_{\mathcal{H}(J')}((I(J) \otimes \rho(J'))H) \quad (5.27)$$

where $\rho(J')$ is the reduced state operator of the complementary subsystem of constituent J , $I(J)$ is the identity operator on the space $\mathcal{H}(J)$ and H is the Hamiltonian operator of the overall composite system. The operator $V(J)$ may be called the *reduced Hamiltonian operator* of the J -th elementary constituent, since for a *separable* constituent it reduces to

$$V(J) = H(J) + \bar{h}(J') \quad (5.28)$$

where

$$\bar{h}(J') = \text{Tr}_{\mathcal{H}(J)}(H(J')\rho(J')) \quad (5.29)$$

is the mean private energy of the complementary subsystem J' (cf. Section 5.1.5, eq. 5.9).

The proposed equation of motion for a general composite system is

$$\frac{d\rho}{dt} = \hat{N}(\rho) = -\frac{i}{\hbar}[H, \rho] - \frac{1}{\hbar^2} \sum_{J=1}^M \tau(J) \{D(J), \rho(J)\} \otimes \rho(J') \quad (5.30)$$

where $\tau(J)$ is the positive time constant characteristic of the J -th elementary constituent, $\rho(J)$ and $\rho(J')$ are the reduced state operators of the J -th elementary constituent and its complementary subsystem, the operator $D(J)$ on $\mathcal{H}(J)$ is defined by the determinant

$$D(J) = \begin{vmatrix} \Delta W(J) & \Delta V(J) & \Delta X(J) & \dots & \Delta Y(J) \\ (V(J), W(J)) & (V(J), V(J)) & (V(J), X(J)) & \dots & (V(J), Y(J)) \\ (X(J), W(J)) & (X(J), V(J)) & (X(J), X(J)) & \dots & (X(J), Y(J)) \\ \dots & \dots & \dots & \dots & \dots \\ (Y(J), W(J)) & (Y(J), V(J)) & (Y(J), X(J)) & \dots & (Y(J), Y(J)) \end{vmatrix}, \quad (5.31)$$

the symbols $\Delta F(J)$ and $(F(J), G(J))$, for $F(J)$ and $G(J)$ any Hermitian operator on the factor Hilbert space $\mathcal{H}(J)$, are defined by

$$\Delta F(J) = F(J) - I(J)\text{Tr}_{\mathcal{H}(J)}(\rho(J)F(J)) \quad (5.32)$$

and

$$(F(J), G(J)) = \text{Tr}_{\mathcal{H}(J)}(\rho(J)\{\Delta F(J), \Delta G(J)\}), \quad (5.33)$$

and

$$W(J) = \text{Tr}_{\mathcal{H}(J')}((I(J) \otimes \rho(J')) \ln \rho). \quad (5.34)$$

It is noteworthy that, if the J -th elementary constituent is in an independent state, then the operator $W(J)$ reduces to

$$W(J) = \ln \rho(J) - \bar{s}(J')/k \quad (5.35)$$

where

$$\bar{s}(J') = -k \text{Tr}_{\mathcal{H}(J')}(\rho(J') \ln \rho(J')) \quad (5.36)$$

is the mean entropy of the complementary subsystem J' (cf. Section 5.1.5, eq. 5.13).

Equation 5.30 defines explicitly the evolution superoperator \hat{N} appearing in the postulates P5QT and P5QST, and completes therefore the paradigms of Quantum Thermodynamics and Quantum Statistical Thermodynamics.

Equation 5.30 generalizes equation 5.16 to systems composed of any number M of distinguishable elementary constituents. If equation 5.16 can be written for each elementary constituent, i.e. if the non-Hamiltonian generators of the motion and the time constant associated with each elementary constituent are given, then equation 5.30 requires no additional input. Thus, the solution of the open problems outlined at the end of Section 5.2.1 implies the solution of the general dynamical problem. Again, the major theorems that follow are independent of the specific types of elementary constituents and apply therefore to the general composite system.

5.2.4 Theorems

The major theorems of the proposed dynamics of a general composite system are as follows. Proofs are given in Appendix C.

Th8QT

If the state operator of the general composite system is

$$\rho = \bigotimes_{J=1}^M P_{\psi}(J), \quad (5.37)$$

where the index J runs over every elementary constituent, then, and only then, the equation of motion 5.30 reduces to the Schrödinger equation of motion, and the evolution of the isolated composite system is therefore purely Hamiltonian.

It is noteworthy that, if the elementary constituents are not all separable, then the initial state 5.37 will evolve into states of different type, eventually triggering the non-Hamiltonian term in the equation of motion.

Th9QT

A physical observable represented by a linear functional c or, equivalently, by a linear Hermitian operator C , is a constant of the motion for the general composite system if, and only if,

- (a) $[C, H] = 0$ and
- (b) C is a linear combination of the operators

$$I, H, X(1) \otimes I(1'), \dots, Y(1) \otimes I(1'), X(2) \otimes I(2'), \dots, Y(M) \otimes I(M')$$

where $I(J)$, $X(J)$, ..., $Y(J)$ are the identity operator and the non-Hamiltonian generators of the motion of the J -th elementary constituent and I , H are the identity operator and the Hamiltonian operator of the overall composite system. It follows that the physical observable represented by the overall Hamiltonian operator H is always a constant of the motion for any isolated physical system. This physical observable is called the *energy* of the system.

Th10QT

The mean value of the entropy increases with time at a rate given by the relation

$$d\bar{s}/dt = \sum_J k \tau(J) g(J) / \hbar^2 \geq 0 \quad (5.38)$$

where $g(J)$ is a positive semi-definite nonlinear functional defined by the following determinant

$$g(J) = \begin{vmatrix} (W(J), W(J)) & (W(J), V(J)) & (W(J), X(J)) & \dots & (W(J), Y(J)) \\ (V(J), W(J)) & (V(J), V(J)) & (V(J), X(J)) & \dots & (V(J), Y(J)) \\ (X(J), W(J)) & (X(J), V(J)) & (X(J), X(J)) & \dots & (X(J), Y(J)) \\ \dots & \dots & \dots & \dots & \dots \\ (Y(J), W(J)) & (Y(J), V(J)) & (Y(J), X(J)) & \dots & (Y(J), Y(J)) \end{vmatrix}. \quad (5.39)$$

This theorem is a statement of existence of irreversible processes for a general isolated physical system. Any such system in any non-equilibrium state tends towards an equilibrium state with the same mean values of the constants of the motion and a higher mean value of the entropy.

Th5QT

Among the states of a system with given mean values of the constants of the motion, one and only one is a stable equilibrium state.

As noted in Section 5.2.2, this is a generalized statement of the second law of Thermodynamics. When the constants of the motion are the energy and the number of particles of constituent species, this theorem coincides with the fourth postulate of the unified quantum theory of Mechanics and Thermodynamics proposed by Hatsopoulos and Gyftopoulos (1976). The first three postulates of their unified quantum theory are equivalent to postulates P1QT through P4QT of Quantum Thermodynamics. Thus, the theorems proved within that theory from the four postulates and the underlying definitions, are also theorems of Quantum Thermodynamics, if the same definitions are adopted.

Th11QT

The explicit expression of the state operator for a general composite system in a stable equilibrium state is

$$\rho = (1/Z) \exp(-\beta H + \gamma_1 C_1 + \dots + \gamma_N C_N) \quad (5.40)$$

where

$$Z = \text{Tr}(\exp(-\beta H + \gamma_1 C_1 + \dots + \gamma_N C_N)) \quad (5.41)$$

and the operators H, C_1, \dots, C_N form a complete and independent set of linear constants of the motion for the composite system. The coefficients $\beta, \gamma_1, \dots, \gamma_N$ are determined by the initial values of the constants of the motion. The function Z can be called the generalized partition function.

Th12QT

The mean value of the entropy of a general composite system in any stable equilibrium state can be written in terms of the mean values of a complete and independent set of constants of the motion and the partition function

$$\bar{s} = k\beta\bar{h} - k\gamma_1\bar{c}_1 - \dots - k\gamma_N\bar{c}_N + k \ln Z. \quad (5.42)$$

This relation can be called the generalized Gibbs equation.

The following theorems refer to subsystems of the general composite system. The notation introduced in Section 5.1.5 is implied.

Th13QT

The causal evolution of the reduced state operator of subsystem K (with elementary constituents indexed by $J(K)$) is determined via the equation of motion (reduced equation of motion)

$$\frac{d\rho(K)}{dt} = -\frac{i}{\hbar} \text{Tr}_{\mathcal{H}(K')}([H, \rho]) - \frac{1}{\hbar^2} \sum_{J(k)=1}^{M(K)} \tau(J(K)) \{D(J(K)), \rho(J(K))\} \otimes \rho(J'(K)). \quad (5.43)$$

Th14QT

Given the reduced equations of motion for the two subsystems K and K' , the equation of motion of the composite system is given by

$$\frac{d\rho}{dt} = \frac{d\rho(K)}{dt} \otimes \rho(K') + \rho(K) \otimes \frac{d\rho(K')}{dt} \quad (5.44)$$

if, and only if, the two subsystems are *separable* and in *independent* states.

The rate of entropy production of a system composed of two subsystems K and K' in *independent* states equals the sum of the corresponding rates of private entropy production if, and only if, the two subsystems are *separable*. Then, and only then,

$$d\bar{s}/dt = d\bar{s}(K)/dt + d\bar{s}(K')/dt. \quad (5.45)$$

Thus, two *separable* systems that are initially *independent* remain independent indefinitely.

We conclude with some qualitative remarks on the notion of reversibility. By virtue of theorem Th10QT, the equation of motion 5.30 is fundamentally irreversible. If the time constants τ are nonzero for “all” elementary constituents, then no material system evolves according to pure Hamiltonian dynamics and there exists no material system with an inherent dynamical behaviour which is purely reversible. Reversible processes, however, can be conceived as the result of either special initial conditions or special limiting situations. For example, eq. 5.37 identifies a special initial condition for which the evolution is initially purely Hamiltonian. Special limiting situations in which the reversible behaviour is approximated, may be verified when the interaction between the constituents of the system are so “strong” that the Hamiltonian term in the equation of motion dominates and overwhelms, for a “short” time, the effect of the irreversible non-Hamiltonian term. Again, for states that are very “close” to stable equilibrium, the non-Hamiltonian contribution may be so small that its “linearization” may become a reasonable approximation. A promising ground is immediately open for a fundamental justification of the successful phenomenological theory of linear irreversible phenomena based on the well known Onsager relations.

These qualitative comments show that the proposed equation of motion has opened several new avenues for further fundamental studies, the theoretical and practical importance of which need not be mentioned.

Chapter 6

SUMMARY AND RECOMMENDATIONS

The purpose of this dissertation has been to present a general quantum theory in which two fundamental problems of contemporary quantum physics find a consistent solution: the lack of a complete equation of motion and the lack of an unambiguous quantum statistical theory.

Quantum Thermodynamics, the physical part of the proposed theory, resolves the incompleteness of the current dynamical theory by introducing a new nonlinear equation of motion (eq. 5.30). The major implications of Quantum Thermodynamics can be summarized as follows: the proposed equation of motion reduces to the Schrödinger equation of motion for a particular class of states; among the states of a system with given mean values of the constants of the motion there exist many equilibrium states, however, one and only one is a stable equilibrium state (this is a generalization of a known statement of the second law of Thermodynamics); any isolated system in any non-equilibrium state evolves towards states of higher entropy (this is a statement of existence of irreversible processes for isolated systems). It is worth stressing that Quantum Thermodynamics is concerned only with a description of the states of any individual physical system and their causal evolution. It is not a statistical theory. In Quantum Thermodynamics, the laws of Thermodynamics and irreversibility emerge as exact consequences of the fundamental quantum *dynamical* behaviour of the elementary constituents of any individual material system, microscopic or macroscopic, simple or complex. This general statement is a major conclusion of the dissertation.

Quantum Statistical Thermodynamics, the statistical part of the proposed theory, resolves the present lack of an unambiguous quantum statistical theory by adopting a new measure-theoretic description of ensembles. This statistical theory is superimposed to and consistent with the laws of Quantum Thermodynamics. It is concerned with the description of stochastic distributions of states in an ensemble of identical systems, each of which individually obeys the laws of Quantum Thermodynamics. To every such ensemble, Quantum Statistical Thermodynamics associates a measure-theoretic descriptor, called the statistical-weight measure, which represents the distribution of individual quantum thermodynamical states in the ensemble. The proposed description is unambiguous in that, for any given ensemble, it uniquely identifies both the spectrum of states represented in the ensemble and their relative population. In other words, it accounts unambiguously for the essential distinction between quantal and nonquantal uncertainties.

Many interesting problems arise from the present work and require further investigation.

The new equation of motion proposed for Quantum Thermodynamics opens a large number of questions and routes of theoretical and experimental investigation. First of all, the non-Hamiltonian generators of the motion and the time constant associated with each type of elementary constituent have been left unspecified. Their specification is an open problem the solution of which will probably require a constructive confrontation between conventional quantum theory, the present theory and the results of past and newly designed experiments. This confrontation will also decide upon the validity of the proposed equation to describe irreversible phenomena. Other theoretical problems consist of deriving from Quantum Thermodynamics more detailed theorems that will help to clarify the physical significance of the underlying nonlinear dynamics. For example, the description of known reversible processes of the type mentioned in Section 5.1.1 point (b), is still an unsolved problem. We have only conjectured that reversible processes may be suitably approximated under special limiting conditions, but we have not explicitly identified such conditions.

The methods of the so-called linear irreversible phenomenological thermodynamics, based on the well known Onsager reciprocity relations, are known to successfully describe a certain class of irreversible phenomena. Also the Boltzmann equation of the kinetic theory of gases is known to describe successfully a certain class of irreversible processes. Yet, both the Onsager relations and the Boltzmann equation cannot be rigorously derived from conventional Hamiltonian dynamics, since that dynamics is fundamentally reversible. The proposed nonlinear irreversible dynamics is instead fundamentally irreversible, and holds the promise to provide a unique fundamental ground for a rigorous derivation of the Onsager relations and the Boltzmann equation.

Finally, application of the proposed dynamical theory to practical problems of physics and engineering is at this moment a most challenging prospect.

As regards Quantum Statistical Thermodynamics, the novel measure-theoretic description of ensembles or, equivalently, of preparations, has introduced two problems. The first problem concerns the empirical determination of the statistical-weight measure describing the preparation under consideration. We have conjectured a possible form of a “quorum” of physical observables the experimental determination of which might prove sufficient to determine uniquely the statistical-weight measure (Section 4.2.3). However, even if this conjecture or a generalization of it were proved, the important physical problem to attach a definite physical and operational meaning to the observables in such a “quorum” would still remain a challenge. The second problem pertains to the domain of Information Theory. We have studied, in the context of Quantum Statistical Thermodynamics, three typical problems of Information Theory and found satisfactory answers only for the particular case in which the spectrum of the statistical-weight measure is known and countable. The more general case in which the spectrum is unknown or noncountable leads to difficulties and requires further analysis.

Appendix A

AMBIGUOUS DESCRIPTIONS OF HETEROGENEOUS PREPARATIONS

This Appendix reports two unsuccessful attempts to obtain a mathematical description of heterogeneous preparations reflecting unambiguously the concept of state of an individual system. The first, based on a description by means of a statistical operator, is found not to satisfy both condition (ii) and (iii) of Section 3.2.3. The second, based on the description by means of a statistical superoperator, is found not to satisfy condition (iii).

A.1 Description by means of a Statistical Operator

Consider a heterogeneous preparation, defined by the symbolic expression

$$\Pi = \sum_n w_n \Pi_n$$

where the component preparations Π_n are homogeneous. Let us attempt to describe such a preparation by means of a statistical operator W (linear, Hermitian, nonnegative-definite and unit-trace) defined on the Hilbert space of the system. To do so we can adopt postulates P2QSM and P3QSM of Section 3.2.2, so that the statistical operator W is linked to the expected mean values of physical observables according to the relation

$$\langle \bar{g} \rangle = \text{Tr}(WG). \quad (3.11)$$

Because the structure of the given heterogeneous preparation is specified, the *expected mean value* $\langle \bar{g} \rangle$ must equal the weighted sum of *mean values* \bar{g}_n corresponding to the homogeneous component preparations Π_n . This condition, i.e.

$$\text{Tr}(WG) = \langle \bar{g} \rangle = \sum_n w_n \bar{g}_n = \sum_n w_n \text{Tr}(\rho_n G), \quad (\text{A.1})$$

is satisfied for all operators G if, and only if,

$$W = \sum_n w_n \rho_n \quad (\text{A.2})$$

Equation A.2 defines the rule of composition required by condition (i) of the Section 3.2.3. However, the description of preparations by means of a statistical operator leads to two types of ambiguities.

The first ambiguity arises from the failure to satisfy condition (ii). The set of irreducible statistical operators (the idempotent statistical operators) is in one-to-one correspondence to the set of idempotent state operators. Thus, the set of irreducible statistical operators is not mathematically rich enough to identify unambiguously all the distinct homogeneous preparations contemplated in Quantum Thermodynamics, i.e. all state operators. In other words, a statistical theory superimposed to Quantum Thermodynamics and based on such a description of preparations could not reproduce the rule of correspondence between states and homogeneous preparations.

The second ambiguity arises from the failure to satisfy condition (iii). This is due to the mathematical fact that the statistical operator W can be resolved into an infinity of weighted sums of *different* state operators, such as

$$W = \sum_n w_n \rho_n = \sum_q w'_q \rho'_q = \dots \quad (\text{A.3})$$

The ambiguity concerns the notion of state of an individual system. From the above multiple decomposition and postulate P4QT of Quantum Thermodynamics (Section 4.1.1), a logical conclusion would be that an individual system prepared according to the scheme Π is, for example, in state ρ_n with probability w_n and, at the same time, in state ρ'_q with probability w'_q . Analogously to what seen in Section 3.2.2, such a system would be a *quantum monster*, i. e. a *single* individual system which is concurrently "in" *two different* states.

We conclude that the mathematical description of heterogeneous preparations by means of a statistical operator is inadequate, inconsistent and ultimately leads to paradoxes.

A.2 Description by means of a Statistical Superoperator

Next we consider an unsuccessful, but instructive, attempt to find an unambiguous mathematical description of heterogeneous preparations. The approach is based on an extension of the axiomatic formulation of Quantum Statistical Mechanics to the next higher mathematical level. Unfortunately, such formulation is found to be ambiguous in that condition (iii) of Section 3.2.3 is not satisfied. In fact, the approach is based on the erroneous hypothesis that the paradigm of Quantum Statistical Mechanics (that we reviewed in Section 3.2.2) is a correct way to superimpose a statistical theory to Quantum Mechanics.

The approach consists of proceeding by mathematical analogy and superimpose a statistical theory to Quantum Thermodynamics. Let \mathcal{H} be the Hilbert space of the system of interest. Let \mathcal{L} , be the *real* space of linear, Hermitian operators on \mathcal{H} . Points (or "vectors") in this space are operators on \mathcal{H} . A state operator on \mathcal{H} , the state descriptor in Quantum Thermodynamics, is therefore a vector in \mathcal{L} . This is analogous to the fact that the state descriptor in Quantum Mechanics is a vector in \mathcal{H} . The analogy then leads to assume that linear, symmetric operators $\overline{G}, \overline{H}, \dots$ defined on \mathcal{L} (superoperators on \mathcal{H}) correspond to physical observables of the system and, more importantly, that the mathematical correspondent of a generic preparation scheme Π is a linear, symmetric, nonnegative-definite, unit-(super)trace operator \hat{W} defined on \mathcal{L} : the direct analogous of the statistical operator W of Quantum Statistical Mechanics. The operator \hat{W} (a superoperator on \mathcal{L}) would be called the *statistical superoperator* and would be linked to the expected mean value $\langle \overline{g} \rangle$ of an observable \hat{G} via evaluation of the (super)trace functional

$$\langle \overline{g} \rangle = \hat{\text{Tr}}(\hat{W}\hat{G}) . \quad (\text{A.4})$$

An analysis of this mathematical description in the light of the conditions of Section 3.2.3 is in order. Condition (i) is satisfied by defining the following rule of composition of different statistical superoperators

$$\hat{W} = \sum_n w_n \hat{W}_n. \quad (\text{A.5})$$

Condition (ii) is also satisfied, and this is a partial success of the approach. The set of statistical superoperators contains in fact irreducible elements that are not decomposable into a weighted sum of *different* statistical superoperators. The typical irreducible element is an idempotent statistical superoperator \hat{P}_A , i.e. a projection (super)operator onto the one-dimensional subspace of \mathcal{L} spanned by operator A . The class of irreducible elements is mathematically rich enough to describe all the possible homogeneous preparations, since it is possible to define the correspondence

$$\rho = A^2 \quad (\text{A.6})$$

from the set of irreducible statistical superoperators to the set of state operators.

The description fails however to satisfy condition (iii) and is therefore ambiguous. The ambiguity originates from the fact that a non-idempotent statistical superoperator \hat{W} can be resolved into an infinity of weighted sums of *different* sets of projection superoperators, such as

$$\hat{W} = \sum_n w_n \hat{P}_{A_n} = \sum_q w'_q \hat{P}_{A_q} = \dots \quad (\text{A.7})$$

The reasons why the non-uniqueness of resolution of the mathematical descriptor of a heterogeneous preparation leads to ambiguities have been already analysed in the last Section and in Section 3.2.2.

We conclude that the mathematical description of heterogeneous preparations by means of a statistical superoperator \hat{W} is inconsistent and ultimately leads to paradoxes.

Appendix B

GENERALIZED LINEAR DYNAMICS

This Appendix considers possible generalizations of Hamiltonian dynamics based on equations of motion of the type

$$\frac{d\rho}{dt} = \hat{L}(\rho) \quad (5.5)$$

where the evolution superoperator \hat{L} is linear in the state operator, i.e.

$$\hat{L}(a_1\rho_1 + a_2\rho_2) = a_1\hat{L}(\rho_1) + a_2\hat{L}(\rho_2) \quad (B.1)$$

for all state operators ρ_1, ρ_2 and for all scalars a_1, a_2 .

B.1 Kossakowski-Lindblad Linear Superoperator

In order to qualify as a bona fide evolution superoperator, \hat{L} must satisfy a number of necessary and sufficient conditions that have first been stated by A. Kossakowski (1972a). Kossakowski (1972b), for a special case, and G. Lindblad (1976), for the general case, have shown that the most general linear superoperator \hat{L} satisfying such conditions is

$$\hat{L}(\rho) = \hat{L}_o(\rho) + \sum_j \hat{L}_j(\rho) \quad (B.2)$$

where

$$\hat{L}_o(\rho) = i[B, \rho], \quad (B.3a)$$

$$\hat{L}_j(\rho) = A_j^\dagger \rho A_j - \frac{1}{2}\{A_j^\dagger A_j, \rho\}, \quad (B.3b)$$

the operator B is Hermitian and the operators A_j (A_j^\dagger indicates the Hermitian conjugate) are instead not necessarily Hermitian. We call \hat{L} the $K - L$ (Kossakowski-Lindblad) superoperator.

For the purposes of Quantum Thermodynamics, this form of the $K - L$ superoperator is still too unrestricted. Since the object of study of Quantum Thermodynamics is the isolated system, we must at least require that the mean value of the physical observable energy be conserved and the mean value of the physical observable entropy be never decreasing.

B.2 Energy Conservation and Entropy Production

The condition that the mean value of the energy of an isolated system be conserved, imposes restrictions on the choice of the operators B and A_j appearing in the definition of the $K - L$ superoperator. The condition is that, for any state operator,

$$d\bar{h}/dt = \text{Tr}(H(d\rho/dt)) = \text{Tr}(H\hat{L}(\rho)) = 0 \quad (\text{B.4})$$

where H is the Hamiltonian operator of the system. By substituting the expression for \hat{L} , we find that the condition is satisfied if, and only if,

$$i[H, B] + \sum_j [A_j, HA_j^\dagger] = 0. \quad (\text{B.5})$$

An obvious choice for B is $B = -H/\hbar$, so that the superoperator \hat{L}_o becomes the Liouvillian (eq. 5.3). However, the choice of the operators A_j is not obvious, especially in view of the next condition.

The condition that the mean value of the entropy of an isolated system be never decreasing imposes restrictions on the choice of the operators A_j defining the $K - L$ superoperator. The condition is that, for any state operator,

$$d\bar{s}/dt = -k\text{Tr}((d\rho/dt) \ln \rho) = -k\text{Tr}(\hat{L}(\rho) \ln \rho) \geq 0. \quad (\text{B.6})$$

By substituting the expression for \hat{L} , we find that the condition becomes

$$d\bar{s}/dt = k \sum_j \text{Tr}(A_j^\dagger A_j \rho \ln \rho - A_j^\dagger \rho A_j \ln \rho) \geq 0 \quad (\text{B.7a})$$

or

$$d\bar{s}/dt = k \sum_{jin} (A_j^\dagger)_{in} (A_j)_{ni} (\rho_i - \rho_n) \ln \rho_i \geq 0 \quad (\text{B.7b})$$

where we have expanded the first expression with respect to an eigenbasis of the state operator. Since the operators A_j cannot depend on the state operator (by the linearity of the $K - L$ superoperator), it follows that for any *singular* state operator (i.e., such that at least one eigenvalue is zero), the rate of entropy production is *infinite*. We find this feature of any linear equation of this type undesirable, since it would imply that a large class of states (including all the states considered in Quantum Mechanics) are highly unstable and evolve towards more stable states at an infinite rate. This observation, added to the general observation made by Simmons about the inadequacy of linear dynamics (cf. Section 5.1.2), has led us to consider nonlinear evolution superoperators. However, an interesting example of linear equation of motion is noteworthy.

B.3 Pauli Master Equation

A particular choice of the operators A_j , which in general does not satisfy the conditions just specified, leads to the famous Pauli master equation. Let us substitute the index j with the double index rs and let

$$A_j = A_{rs} = c_{rs}|r\rangle\langle s| \quad (A_{rs}^\dagger = c_{rs}^*|r\rangle\langle s|) \quad (\text{B.8})$$

where the vectors $|i\rangle$ form an eigenbasis belonging to the Hamiltonian operator, $|i\rangle\langle j|$ are the corresponding dyadic operators and c_{rs} are complex scalars. The corresponding equation of motion becomes

$$\frac{d\rho}{dt} = -\frac{i}{\hbar}[H, \rho] + \sum_{rs} c_{rs} c_{rs}^* (\rho_{rr} |s\rangle\langle s| - \frac{1}{2} \{|s\rangle\langle s|, \rho\}) . \quad (\text{B.9})$$

Letting $c_{rs} c_{rs}^* = w_{rs}$ (clearly, $w_{rs} \geq 0$) and taking the ij -th matrix element of the equation with respect to the same Hamiltonian eigenbasis, we obtain the master equation

$$\frac{D\rho_{ij}}{Dt} = \delta_{ij} \sum_r w_{ir} \rho_{rr} - \rho_{ij} \frac{1}{2} \sum_r (w_{ri} + w_{rj}) \quad (\text{B.10})$$

where we defined

$$\frac{D\rho_{ij}}{Dt} = \frac{d\rho_{ij}}{dt} + \frac{i}{\hbar} \rho_{ij} (E_i - E_j) . \quad (\text{B.11})$$

For state operators that commute with the Hamiltonian H , the eigenvalues p_i of the state operator vary according to the equation

$$\frac{dp_i}{dt} = \sum_r w_{ir} p_r - p_i \sum_r w_{ri} . \quad (\text{B.12})$$

In order for the Pauli master equation to be energy conserving, the following condition must be satisfied

$$\sum_j [A_j, H A_j^\dagger] = \sum_{rs} w_{rs} E_s (|r\rangle\langle r| - |s\rangle\langle s|) = 0 \quad (\text{B.13})$$

or, by taking matrix elements, the condition

$$\sum_s (w_{ns} E_s - w_{sn} E_n) = 0 \quad (\text{B.14})$$

must be satisfied for every n . The entropy production condition is

$$d\bar{s}/dt = k \sum_{rs} w_{rs} (\rho_{rr} - \rho_{ss}) \ln \rho_{ss} \geq 0 . \quad (\text{B.15})$$

We see that the energy conservation and entropy production requirements impose very restrictive conditions on the coefficients w_{rs} . If we set $w_{rs} = w_{sr}$, to satisfy the entropy condition, then the energy condition imposes that $w_{rs} = w \delta_{rs}$. The equation of motion then becomes

$$\frac{D\rho_{ij}}{Dt} = w (\delta_{ij} \rho_{ii} - \rho_{ij}) \quad (\text{B.16})$$

or

$$\frac{D\rho}{Dt} = w \left(\sum_i |i\rangle \rho_{ii} \langle i| - \rho \right) . \quad (\text{B.17})$$

This equation satisfies the energy conservation and entropy production requirements, however, it is no exception to Simmon's observation and the observation about infinite entropy production for singular state operators.

To conclude, we present another example of linear equation which satisfies the energy and the entropy conditions. Let the set of operators A_j be composed of the Hermitian operator $i\tau^{\frac{1}{2}}F/\hbar$ only, where τ is a positive time constant and $[F, H] = 0$. The corresponding equation is

$$\frac{d\rho}{dt} = -\frac{i}{\hbar}[H, \rho] - \frac{\tau}{2\hbar^2}[F, [F, \rho]]. \quad (\text{B.18})$$

This equation has already been considered by Park and Band (1978).

Appendix C

PROOFS OF MAJOR THEOREMS OF QUANTUM THERMODYNAMICS

This Appendix outlines the proofs of the major theorems of Quantum Thermodynamics that are enounced in Chapter 5.

Th1QT

Let the state operator be a projection operator and substitute into eq. 5.16. The first term of the equation results in eq. 5.1 which is totally equivalent to the Schrödinger equation of motion. The second term of eq. 5.16 vanishes. To see this, we observe that the operator $P_\psi \ln P_\psi$ is the null operator, therefore, by the definition 5.19, all the scalar products in the first column of 5.17 vanish. The first entry of the column does not vanish but becomes the null operator when D is inserted into eq. 5.16.

Th2QT

The rate of change of the mean value of an observable represented by the Hermitian operator C , i.e.

$$\text{Tr}(C(d\rho/dt)), \quad (\text{C.1})$$

is given by

$$(-i/\hbar)\text{Tr}(\rho[H, C]) - (\tau/\hbar^2) \begin{vmatrix} (C, \ln \rho) & (C, H) & (C, X) & \dots & (C, Y) \\ (H, \ln \rho) & (H, H) & (H, X) & \dots & (H, Y) \\ (X, \ln \rho) & (X, H) & (X, X) & \dots & (X, Y) \\ \dots & \dots & \dots & \dots & \dots \\ (Y, \ln \rho) & (Y, H) & (Y, X) & \dots & (Y, Y) \end{vmatrix} \quad (\text{C.2})$$

where we substituted eq. 5.16 into eq. C.1 and used eqs. 5.18 and 5.19. For C to represent a linear constant of the motion, eq. C.2 must vanish for any state operator. The first term in the equation requires that C commute with H . In order for the determinant in the second term of eq. C.2 to vanish for any state operator it is necessary and sufficient that a row (column) is either a linear combination of the other rows (columns) or else it vanishes. By the definitions 5.18 and 5.19, the first row vanishes if C is proportional to the identity operator I . Since the generators H, X, \dots, Y are fixed, the only other possibility is that the first row is a linear combination of the other rows. This occurs independently of the state operator only if C is a linear combination of

the generators of the motion (recall that (\cdot, \cdot) is a real scalar product and is therefore linear in each factor). Thus, the second term of eq. C.2 vanishes if and only if

$$C = aI + bH + cX + \dots + dY. \quad (\text{C.3})$$

Since all the generators of the motion commute with H , also the first term vanishes. The possibility that the difference between the first term and the second term in C.2 vanishes independently of the state operator, while the two terms do not vanish individually, is excluded. In fact, with respect to the state operator, the first term is a linear functional while the second is a nonlinear functional, therefore the two functionals cannot be identical independently of the state operator.

Th3QT

The first term of eq. 5.16 vanishes if and only if the state operator commutes with H . Let us assume this is the case. The second term becomes proportional to the operator

$$Q = \begin{vmatrix} \{\rho, \Delta \ln \rho\} & \{\rho, \Delta H\} & \{\rho, \Delta X\} & \dots & \{\rho, \Delta Y\} \\ (H, \ln \rho) & (H, H) & (H, X) & \dots & (H, Y) \\ (X, \ln \rho) & (X, H) & (X, X) & \dots & (X, Y) \\ \dots & \dots & \dots & \dots & \dots \\ (Y, \ln \rho) & (Y, H) & (Y, X) & \dots & (Y, Y) \end{vmatrix}. \quad (\text{C.4})$$

By the properties of determinants, Q is not altered if we subtract from the first column a linear combination of the other columns. We do so by using the same coefficients of eq. 5.21a. By recalling the definition of (\cdot, \cdot) , we obtain

$$Q = \begin{vmatrix} \{\rho, \Delta \ln \rho - \Delta R\} & \{\rho, \Delta H\} & \dots & \{\rho, \Delta Y\} \\ \text{Tr}(\Delta H \{\rho, \Delta \ln \rho - \Delta R\}) & (H, H) & \dots & (H, Y) \\ \text{Tr}(\Delta X \{\rho, \Delta \ln \rho - \Delta R\}) & (X, H) & \dots & (X, Y) \\ \dots & \dots & \dots & \dots \\ \text{Tr}(\Delta Y \{\rho, \Delta \ln \rho - \Delta R\}) & (Y, H) & \dots & (Y, Y) \end{vmatrix}. \quad (\text{C.5})$$

In order for Q to vanish, the first column must vanish, i.e. the operator $\{\rho, \Delta \ln \rho - \Delta R\}$ must be the null operator. This condition holds if and only if ρ commutes with R , in which case the operator becomes

$$2 \sum_i p_i (\ln p_i - R_i - \sum_k p_k (\ln p_k - R_k)) |i\rangle \langle i|$$

where $|i\rangle$ is an eigenbasis shared by ρ and R . It is the null operator if and only if the eigenvalues p_i are either 0 or satisfy equation 5.21c:

$$\ln p_i = R_i - \ln z$$

with

$$-\ln z = \sum_k p_k (\ln p_k - R_k) = \sum_k (1/z) \exp(R_k) (R_k - \ln z - R_k),$$

which reduces to equation 5.21d.

Th4QT

Equation 5.22 is obtained by substituting equation 5.16 into the expression for the rate of entropy production

$$d\bar{s}/dt = -k\text{Tr}((d\rho/dt) \ln \rho) \quad (\text{C.6})$$

and making use of the definitions 5.18 and 5.19. The important inequality follows from the fact that the determinant g defined by equation 5.23 is a Gram determinant with respect to the scalar product (\cdot, \cdot) , and it is known that Gram determinants are positive semi-definite (cf. E.F. Beckenbach and R. Bellman (1965)).

Th5QT

This theorem follows directly from the definition of stable equilibrium state and the fact that such state has the maximum mean value of the entropy for the given mean values of the constants of the motion. A mathematical proof of the existence and uniqueness of such state can be found in A. Katz (1967, pp. 47-50), where, however, the interpretation of the mathematical symbols is radically different from the present.

We conjectured that the statement that we have used to define stable equilibrium state should follow as a theorem of the proposed dynamics and the mathematical definition of stability according to A. Liapunov (1892). In our context, such definition would read as follows.

Definition: Stable Equilibrium States

An equilibrium state operator ρ' is said to represent a stable equilibrium state if, and only if, for any $\varepsilon > 0$ there exists a $\delta > 0$ such that any state operator ρ'' , sharing with ρ' the values of the constants of the motion and such that its *distance* from ρ' is less than δ , evolves according to the equation of motion 5.16 in such a way that its distance from ρ' at any later time remains always less than ε .

Here the *distance* between two state operators ρ' and ρ'' can be defined as

$$d(\rho', \rho'') = \left(\sum_{ij} |\rho'_{ij} - \rho''_{ij}|^2 \right)^{1/2}. \quad (\text{C.7})$$

However, we have not been able to prove this conjecture.

Th6QT

The mathematical proof of this theorem can be found in A. Katz (1967, pp. 45-47). It follows from the maximization of the mean entropy formula subject to the constraint that the state operator have the given mean values of the constants of the motion.

Th7QT

A mathematical proof of this theorem can be found in A. Katz (1967, pp. 50-51).

Th8QT

By substitution of eq. 5.37 into eq. 5.30, the first term of the equation of motion reduces to the Schrödinger equation for the composite system. The second term vanishes. To see this, we observe

that eq. 5.35 holds for the operator $W(J)$ and $\bar{s}(J')$ vanishes. Thus, for each J , the determinant of eq. 5.31 vanishes, the reason being the same as that discussed for theorem Th1QT.

Th9QT

The proof of this theorem is analogous to that of theorem Th2QT, where instead of the single determinant in eq. C.2 there is one determinant for each elementary constituent.

Th10QT

The proof of this theorem is identical to that of theorem Th4QT and follows from the known properties of Gram determinants.

Th11QT

See proof of Th6QT.

Th12QT

See proof of Th7QT.

Th13QT

Equation 5.43 is obtained immediately by partial tracing equation 5.30 over the complementary factor Hilbert space of subsystem K , i.e. over all the factor Hilbert spaces of the elementary constituents that are not contained in subsystem K . That the terms in the sum of equation 5.30 corresponding to such elementary constituents vanish under partial tracing, follows from the fact that the first row of the determinants in eq. 5.31 vanishes under the trace due to definition 5.32.

Th14QT

Consider a system composed of subsystems K and K' . Since the two subsystems are separable and in independent states, equations 5.8, 5.11 and 5.12 hold. By substitution into the first term of eq. 5.30 (the Hamiltonian term), it is seen that such term satisfies eq. 5.44. To see that also the second term satisfies eq. 5.44, we write it as follows

$$\begin{aligned} & \sum_{J(K)=1}^{M(K)} \tau(J(K)) \{D(J(K)), \rho(J(K))\} \otimes \rho(J(K)') + \\ & \sum_{J(K')=1}^{M(K')} \tau(J(K')) \{D(J(K')), \rho(J(K'))\} \otimes \rho(J(K')') \end{aligned} \quad (C.8)$$

and observe that, by eq. 5.11,

$$\begin{aligned} \rho(J(K)') &= \rho(J'(K)) \otimes \rho(K') \\ \rho(J(K')') &= \rho(J'(K')) \otimes \rho(K) \end{aligned} \quad (C.9)$$

Finally, by eqs. 5.8 and 5.12, the determinants $D(J(K))$ (and analogously $D(J(K'))$), as defined by eqs. 5.31-5.34, are identical to the determinants that would be associated with the subsystem K (and K') considered as isolated. Thus, substitution of eq. C.8 into eq. C.9 verifies eq. 5.44.

Th15QT

The if part follows directly from eq. 5.44 and the evaluation of the rate of entropy production (eq. C.6). To prove the only if part assume that the two subsystems are not separable. This means that eq. 5.8 is not verified. Thus, also eq. 5.28 is not verified and the determinants $D(J(K))$ of

eq. C.7 differ from those for subsystem K considered as isolated. Moreover, the Hamiltonian term of eq. 5.30 does not split into two terms, since the two subsystems are interacting. Eq. 5.44 is not verified, therefore, eq. 5.45 does not hold and the subsystems that were initially in independent states evolve into dependent states.

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